# THE THEORY AND USE OF INDICATORS

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# THE THEORY AND USE OF INDICATORS

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## PROBLEMS IN PHYSICAL CHEMISTRY

WITH PRACTICAL APPLICATIONS

With a Preface by

F. G. DONNAN, M.A., PH.D., F.R.S.

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# THE THEORY AND USE OF INDICATORS

AN ACCOUNT OF THE CHEMICAL EQUILIBRIA OF ACIDS, ALKALIES AND INDICATORS IN AQUEOUS SOLUTION, WITH APPLICATIONS

BY

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# PREFACE

While the classification of solutions into acid and alkaline dates back to the dawn of chemical speculation, it was only in the latter part of the nineteenth century that the gap between the two was filled and that a kind of continuity was established between these properties in the case of all aqueous solutions. This continuity is implied by the working hypothesis of an equilibrium between hydrogen and hydroxyl ions, which arose naturally from the results obtained by the application of physical methods to solutions.

The effects of acids and alkalies upon some substances, which are still used as indicators of the presence of hydrion or hydroxylion, also attracted attention early in the history of the arts. Thus, as has been noted in the *Comptes Rendus* for 1916, the Romans tested the "hardness" of drinking water by its bleaching effect upon small quantities of red wine (Hippocrates).

The properties and constitutions of the synthetic compounds now largely used as indicators have been investigated mainly by the more purely chemical methods, and not until comparatively recently by physical methods. The problem of describing the state of, and the changes in, solutions containing indicators can be approached, then, both from the point of view of electrolytic equilibria and also from that of molecular structure, and such solutions have therefore been the subject of most interesting controversies.

It is the purpose of the present work to present to the

student a connected survey in which it may appear that different views of the subject are not necessarily inconsistent with one another, and that, taken together, they form a body of theory which has already given a great power in dealing with, *e.g.*, the problems of physiology, the fermentation industries, and chemical geology.

The book is also addressed to the technical chemist who appreciates the value of working hypotheses. On this account there have been included a selection of the most important formulæ and constants (in excess of those required to illustrate the theories) in order that the hydrion and hydroxylion concentrations of all common aqueous solutions at various temperatures may be calculated with the greatest ease.

On the practical side, sufficient directions have been supplied for the reproduction of all the standards mentioned, and for the testing of indicators, etc., a knowledge of ordinary chemical and physico-chemical manipulation being assumed.

The tabulated lists of indicators and their change points, with the charts and neutralisation curves (on which the hydrogen exponent is reproduced to uniform scale) and the account of the theory of titration, will, it is hoped, aid the analyst in the choice of indicators for various purposes, and in the determination of the accuracy of titrations.

This foreword would not be complete without an acknowledgment of the use which has been made of some outstanding books and monographs (to which the reader is referred for a fuller treatment), and principally the following: — "Die Affinitatsmessungen," H. Lunden Ahrens' Sammlung, XIV.; "Der Stand der Indikatoren Frage," A. Thiel Ahrens' Sammlung, XVI.; "Theoretical Organic Chemistry," Cohen; "Modern Research in Organic Chemistry," Pope; "Die Theorie der Alkalimetrischen und

Azidimetrischen Titrierungen," Niels Bjerrum, Copenhagen, Ahrens' Sammlung, XXI.; "Indikatoren der Acidimetrie und Alkalimetrie," F. Glaser; "Tables of Ionisation Constants," Dr. H. Scudder (Constable), 1914; "Die Wasserstoffionen-Konzentration," Dr. L. Michaelis.

Extensive use has also been made of researches published by: Noyes and co-workers, Sorensen and co-workers, Friedenthal, Salm, Walker and co-workers, Hantzsch and co-workers, B. de Szyszkowsky, Arrhenius, Tizard, Baly and co-workers, Hewitt, Stewart, Tuck, Francis and co-workers, McBain and Bray.

The Author is indebted to Dr. Hildebrand for original diagrams showing some neutralisation curves. The curves of light absorption of indicators in Chap. VIII. have been kindly determined by Mr. A. B. Clark by favour of Dr. C. E. K. Mees, at the laboratories of the Eastman Kodak Company, New York.

E. B. R. P.

1916.

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## CORRIGENDA AND ADDENDA.

Page 4, line 19. *Read* "minimum, when the ratio of $[OH']$ to $[H\cdot]$ is that of the constants expressing the velocities of catalysis by $OH'$ and $H\cdot$. Finally it increases again with the subsequent increase of $[H\cdot]$. An independent determination of the free acid (hence $[H\cdot]$) when taken with the known value of the above ratio gives the value of $K_w$."

Page 7, line 2. "Deviations," *not* "denations."

Page 39, paragraph 5. *For* "Veley" *substitute* "Farmer," and in the second line *read* "and Veley that of ammonium salts."

Page 48. *For* "$-0{\cdot}1775$" *read* "$+0{\cdot}1775$" throughout, and in the third line from bottom *substitute* "$_{s}E_{x}$" *for* "$_{0}E_{x}$."

Page 79, paragraph 4. *Read* "$CuCl_2 \cdot 2H_2O$."

Page 96. Formula on left, *transfer* "$NO_2$" to "para" position.

Page 100. *Delete* one N bond in formula I., and continue both bonds right across benzene ring in II.

Page 104. *For* "$K \times 10^{-7}$" *read* "$K \times 10^{7}$."

Page 105. *For* "p. 1103" *read* "p. 1104."

Page 110. *For* "triamido" *substitute* "triamino."

Page 111. In upper left-hand formula, *for* "$(CH_3)_2H$" *read* "$(CH_3)_2N$."

Page 115. In formula II. *substitute* single bond for double bond on central carbon atom.

Page 116. Formulæ Lactone I. on upper left, *read* "(3)HO," carbon on right joined to nearest point of benzene ring.
Carbinol III. at bottom *read* "ONa(2)."
Quinone II. on upper left *read* "(3)HO."

Page 129. Equation (2), "$[M'_2]$" *not* "$[M'_2]$."

Page 135. Formula. Connect "C" on left with benzene ring. Make upper benzene ring on right identical with that below.

Page 182, line 17. Note to "balanced neutrality,*": "*This effect was early recognised by Moore, Roaf and Whitley, *Proc. Roy. Soc.*, B., vol. 77, 102 (1905). It was determined for blood serum by Moore and Wilson, *Biochem. J.*, I. 297 (1906)."

Page 182, line 4 (from bottom). *Alter* "0·0001" *to* "0·001."

Page 220, line 14 (from bottom). *For* "at" *substitute* "as."

Page 222, line 9 (from bottom). *For* "35·95" *read* "3·595."

Page 254, line 4. *For* "between" *substitute* "of"; line 5, *for* "and" *substitute* "to."

Page 257, line 1. Note to "accuracy,*": "*E.g.*, in this case 0·01 c.c. of the titrant of the normality given."

Page 260, line 2 (from bottom). *Instead of* "and" *read* "acid."

Page 261, line 2. *After* "$[H\cdot]$" *insert* "or $[OH']$."

Page 263, line 3 (from bottom). *For* "$T_AK_A$" *substitute* "$T_aK_a$."

Page 288, last line. *Read* "$= + \frac{T_a}{235}$."

Page 295, line 8 (from bottom). *For* "CO" *read* "$CO_2$."

Page 300, line 1. Note to "Preparation*": "*See also Werner, *J. Chem. Soc.*, 113, 20 (1918)."

Page 361. In Index *insert* "Farmer, 39."

## ADDENDUM.

Note to "balanced neutrality," p. 182: This effect was early recognised by Moore, Roaf and Whitley, *Proc. Roy. Soc.*, B., vol. 77, 102 (1905). It was determined for blood serum by Moore and Wilson, *Biochem. J.*, I. 297 (1906).

# THE THEORY AND USE OF INDICATORS

## CHAPTER I

### ELECTROLYTIC EQUILIBRIA IN WHICH THE HYDROGEN AND HYDROXYL IONS TAKE PART — PHYSICAL METHODS OF DETERMINING HYDRION AND HYDROXYLION CONCENTRATIONS.

General equations of solution equilibrium. The water constant. The calculation of $[H^{\cdot}]$ and $[OH']$ from electrical conductivity. Dissociation constants. The amounts of $H^{\cdot}$ and $OH'$ and other ions in pure acids (bases) and mixtures. Selected tables of dissociation constants and the effect of dilution upon these. Acids (bases) forming di- and multi-valent ions. Deviations from the dilution law. Concentrated solutions. Strong acids and bases. Empirical dissociation constants of these. Tables of the ionisation of strong acids and of alkalies. The general equations of hydrolysis. Experimental methods of determining $[H^{\cdot}]$ and $[OH']$ including: Catalysis. Distribution ratio. Solubility product. The theory and use of the hydrogen electrode. The effect of temperature on the $[H^{\cdot}]$ and $[OH']$ derived from hydrolysed salts and from pure acids and bases.

In its broadest sense the chemical indicator may be defined as a substance which when added in small quantities shows the appearance or disappearance of a chemical individual (ion or molecule) by a conspicuous change of colour. In this volume only those indicators will be described which show the presence of hydrion or hydroxylion ($H^{\cdot}$ or $OH'$), in other words, the indicators of acidimetry and alkalimetry.

The study of indicators is chiefly interesting from three points of view. In the first place there is the practical question of their sensitivity, *i.e.*, the accuracy with which

they can be used for titrations and colorimetric estimations. In the second place they can be used in the investigation of the H· and OH′ equilibria in which they play a part. Conversely, an independent study of the H· and OH′ equilibrium is necessary, preliminary to the scientific theory of indicators.

Thirdly, there is the question as to the relation between colour change and constitution.

The last two questions have been to some extent considered separately in the early chapters.

A consistent description of the interaction of acids and bases can be given by the ionic hypothesis, and it is therefore necessary at the outset to give an account of this as applied to the hydrogen and hydroxyl equilibrium. The ions H· and OH′ are always present, if only to a minimal extent in aqueous solutions, and the water molecules $H_2O$ $(H_2O)_2$ or $(H_2O)_3$ are also present in very high concentration, which for many purposes may be considered as constant.

The concentrations of other molecules or ions present are regulated by equations (1) and (2) respectively :—

$$n_1A_1 + n_2A_2 \ . \ . \ . \rightleftarrows n_1'A_1' + n_2'A_2' \ . \ . \ .$$
$$\frac{A_1^{n_1} \times A_2^{n_2} \ . \ . \ .}{A_1'^{n_1'} \times A_2'^{n_2'} \ . \ . \ .} = K \quad . \quad . \quad . \quad (1)$$

$$n_1A_1^{+} + n_2A_2^{-} \ . \ . \ . \rightleftarrows n_1'A_1'^{+} + n_2'A_2'^{-} \ . \ . \ .$$
$$\frac{[A_1^{+}]^{n_1} \times [A_2^{-}]^{n_2} \ . \ . \ .}{[A_1'^{+}]^{n_1'} \times [A_2'^{-}]^{n_2'}} = K \quad . \quad . \quad (2)$$

The symbols have the usual significance. A, etc., are the molecules, $A_1^{+}$, etc., the anions, $A_2^{-}$, etc., the kathions.*

$n_1$, etc., are the numerical coefficients of the equations of reaction, and square brackets signify the concentration of

* In what follows the anion is denoted by the symbol ′, the kathion by · ; the reactions which occur in practice are a mixture of types (1) and (2).

the enclosed molecule or ion. The ionic concentrations are further defined by the law of electrical neutrality whereby—

$$[A_1'] + [A_3'] = [A_2'] + [A_4'] *$$

the concentrations being expressed in equivalents.

In solution equilibria usually both charged and uncharged molecules and ions take part, and these are probably hydrated to different extents. Thus, the complete mathematical relations between the chemical individuals and complexes are no doubt sufficiently complicated in solutions of even the simplest, *i.e.*, binary electrolytes. Yet there are a number of approximations which allow easy calculations of great practical utility to be made.

The equations of homogeneous equilibrium for a binary electrolyte (A = acid element or radicle, B = basic element or radicle) are as follows :—

| | | | |
|---|---|---|---|
| Salt | $[A'] \times [B\cdot] = K_S[AB]$ | . . | (1) |
| Acid | $[A'] \times [H\cdot] = K_A[AH]$ | . . | (2) |
| Base | $[B\cdot] \times [OH'] = K_B[BOH]$ | . . | (3) |
| Water | $[H\cdot] \times [OH'] = K_W[H_2O]$ | . . | (4) |

If the equilibrium is heterogeneous, *i.e.*, if one of the chemical individuals is present not only in solution but also either (*a*) as a solid or (*b*) as a gas at constant pressure, then the concentration of this substance is supposed to be constant, and in equilibrium with a constant product of ionic concentrations. The constancy of the "solubility product" has been verified in many cases. In homogeneous solution also the product is constant of those ions which are in equilibrium with a very high and therefore approximately constant molecular concentration.

Thus the concentration of $H_2O$ in solutions of ordinary

* The left-hand side of this equation includes of course all the kathions on both sides of (2), and the right all the anions.

concentration is practically unalterable by any alteration in the hydrolysis, &c.

Therefore the ionic product $[H^{\cdot}] \times [OH'] = K'[H_2O]$ is taken as constant and known as the " water constant " $K_w$.

The numerical value of $K_w$ has been found by the following methods :—

(1) By the conductivity of the purest water (Kohlrausch and Heydweiller). In this the electric current can only be carried by $H^{\cdot}$ and $OH'$ derived from the dissociation of the water itself. Hence, as the mobilities of these ions are known from these conductivities of acids and bases (see p. 9) their concentrations in the water can be calculated.

(2) By the effect of $H^{\cdot}$ and $OH'$ in catalysing the hydrolysis of ethyl acetate (Wijs),

$$CH_3{\cdot}CO(OC_2H_5) + H_2O = C_2H_5{\cdot}OH + CH_3{\cdot}COOH.$$

The $OH'$ ion has a more powerful effect than the $H^{\cdot}$ and the former is continually diminished by the formation of acetic acid. The velocity therefore falls off and reaches a minimum when $[H^{\cdot}]$ and $[OH']$ are at a minimum, *i.e.*, at the neutral point. Finally, it increases again with the subsequent increase of $[H^{\cdot}]$. A comparison of the velocity at the minimum with that brought about by a known $[OH']$ gives the $[OH']$ at absolute neutrality, and therefore since $[H^{\cdot}] \times [OH'] = [OH']^2 = K_w$, the value of $K_w$.

(3) By the electromotive force of the hydrogen electrode in an acid-alkali cell (Ostwald, Arrhenius, Nernst). By this means $[H^{\cdot}]$ of the alkaline solution may be found (see p. 41 *et seq.*), and $[OH']$ is known from the alkali concentration and degree of dissociation, hence $[H^{\cdot}] \times [OH']$ in alkali, which is equal to $[H^{\cdot}] \times [OH']$ in pure water.

(4) By the determination of the degree of hydrolysis of the salts of acids and bases of which the dissociation constants are independently known. Conversely every calcula-

tion of the acidity and alkalinity which is made with the accepted values of $K_w$, and which agrees with $[H^·]$ or $[OH']$ experimentally determined is a further confirmation of the value of $K_w$ (see Hydrolysis, p. 29).

The values of $K_w$ have been converted to 18° by Sorensen. The agreement is good, considering the diversity of the methods and the number of assumptions and corrections involved in some of them.

| | $K_w \times 10^{14}$ |
|---|---|
| Hydrolysis of sodium acetate (Arrhenius, Shields, *Zeitsch. phys. Chem.*, 11, 823 (1893)) . . | 0·73 |
| Conductivity of the purest water (Kohlrausch and Heydweiller, *Zeitsch. phys. Chem.*, 14, 317 (1894)) | 0·63 |
| Saponification of methyl acetate (Van't Hoff and Wijs, *Zeitsch. phys. Chem.*, 11, 492 (1893); 12, 514 (1893)) . . . . . | 0·83 |
| Electromotive force of the hydrogen electrode in the acid-alkali cell (Ostwald, Nernst, *Zeitsch. phys. Chem.*, 11, 521 (1893); 14, 155 (1894)) . | 0·64 |
| Electromotive force of the hydrogen electrode in dilute acid and alkali (Lowenherz, *Zeitsch. phys. Chem.*, 20, 283 (1896)) . . . . | 0·74 |
| Hydrolysis of the ammonium salt of diketotetrahydrothiazol (Kundt) . . . . . | 0·46 |
| Hydrolysis of the trimethyl pyridine salt of paranitrophenol (Lunden) . . . . . | 0·61 |
| Electromotive force of the hydrogen electrode against N/10KCl HgCl electrode (see pp. 49 to 53) (Sorensen, *Biochem. Zeitsch.*, 21, 131 (1909)) . . . . . | 0·72 |

From all these values, it was estimated that the most probable at 18° is

$$K_w = 0{\cdot}73 \times 10^{-14}$$

or in exponential notation

$$K_w = 10^{-14\cdot14}.$$

And $$[H^{\cdot}] = [OH'] = 0\cdot85 \times 10^{-7}$$

or $$= 10^{-7\cdot07}.$$

*Change of $K_w$ with Temperature.*

The water constant changes rapidly with the temperature as may be seen from the following tables :—

| $t°$ C. | $K_W \times 10^{14}$ (i.) | (ii.) | (iii.) | (iv.) |
|---|---|---|---|---|
| 0 | 0·12 | 0·14 | 0·089 | |
| 18 | 0·59 | 0·72 | 0·46 | 0·62 |
| 25 | 1·04 | 1·22 | 0·82 | 1·05 |
| 50 | 5·66 | 8·8 | | 5·17 |
| 100 | 58·2 | 74·0 | 48·0 | |

(i.) Kohlrausch and Heydweiller (Conductivity), Heydweiller, *Ann. der Phys.*, (4) 28, 512 (1909).

(ii.) Lorenz and Bohi (Electromotive force), *Zeitsch. phys. Chem.*, 66, 733 (1909).

(iii.) Noyes and Collaborators (Conductivity of hydrolysed salts).

The following tables contain some complete series of results :—

Noyes—

| $t°$ = | 0 | 18 | 25 | 100 | 156 | 218 | 306 |
|---|---|---|---|---|---|---|---|
| $K_w \times 10^{14}$ = | 0·089 | 0·46 | 0·82 | 48·0 | 223·0 | 461·0 | 168 |
| $[H^{\cdot}] \times 10^{7}$ = | 0·30 | 0·68 | 0·91 | 6·9 | 14·9 | 21·5 | 13·0 |

Lorenz and Bohi—

| $t°$ = | 0 | 18 | 25 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 99 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $10^{14}K_w$ = | 0·14 | 0·72 | 1·22 | 1·74 | 3·82 | 8·8 | 12·8 | 21·5 | 35·0 | 53·5 | 72·0 |
| $10^{7}[H^{\cdot}]$ = | 0·37 | 0·85 | 1·10 | 1·32 | 1·98 | 2·96 | 3·55 | 4·61 | 5·92 | 7·30 | 8·49 |
| $10^{7}[H^{\cdot}]$ = | 0·37 | 0·85 | 1·12 | 1·36 | 1·93 | 2·66 | 3·55 | 4·61 | 5·84 | 7·23 | 8·60 |

(calculated).

The experimental values (middle row) show positive and negative denations from a regular curve, especially at the higher temperatures. The smoothed values (lower row) are derived from the heat of dissociation according to p. 60.

The following values have been determined recently by Michaelis, using the hydrogen electrode method with careful correction for diffusion potentials ("Die Wasserstoffionen, Konzentration," p. 8).

| $t°$ C. | Log. $K_W$. | $10^{14}\ K_W$. | $10^7 \sqrt{K_W}$. |
|---|---|---|---|
| 16 | 14·200 | 0·63 | 0·79 |
| 17 | 14·165 | 0·68 | 0·82 |
| 18 | 14·130 | 0·74 | 0·86 |
| 19 | 14·100 | 0·79 | 0·89 |
| 20 | 14·065 | 0·86 | 0·93 |
| 21 | 14·030 | 0·93 | 0·96 |
| 22 | 13·995 | 1·01 | 1·005 |
| 23 | 13·960 | 1·10 | 1·05 |
| 24 | 13·925 | 1·19 | 1·09 |
| 25 | 13·895 | 1·27 | 1·13 |
| 26 | 13·860 | 1·38 | 1·17 |
| 27 | 13·825 | 1·50 | 1·23 |
| 28 | 13·790 | 1·62 | 1·27 |
| 29 | 13·755 | 1·76 | 1·33 |
| 30 | 13·725 | 1·89 | 1·37 |
| 31 | 13·690 | 2·04 | 1·43 |
| 32 | 13·660 | 2·19 | 1·48 |
| 33 | 13·630 | 2·35 | 1·53 |
| 34 | 13·600 | 2·51 | 1·59 |
| 35 | 13·567 | 2·71 | 1·65 |
| 36 | 13·535 | 2·92 | 1·71 |
| 37 | 13·505 | 3·13 | 1·77 |
| 38 | 13·475 | 3·35 | 1·83 |
| 39 | 13·445 | 3·59 | 1·89 |
| 40 | 13·420 | 3·80 | 1·95 |

The concentrations of $H^{\cdot}$ and $OH'$ present in pure water, although low, are thus quite definite. If the number of individual molecules in a mol is taken as $70 \times 10^{22}$, then at a temperature of 22° at which $K_W = 1 \times 10^{-14}$, 1 mol or 18 grams of water contains $70 \times 10^{22} \times 10^{-7}$ or $70 \times 10^{15}$ molecules of each ion.

A consequence of the constancy of $K_W$ is that all aqueous solutions contain both $H^{\cdot}$ and $OH'$, and if one of these is known the other can be calculated. Hence it is not necessary to state both the acidity and alkalinity of an acid or alkaline solution, but only its acidity or hydrion concentration $[H^{\cdot}]$. Even the exceedingly small $[H^{\cdot}]$ of an alkaline solution is perfectly definite, as is shown by the fact that it gives a steady E.M.F. with the hydrogen electrode, which is in accordance with the logarithmic law. The product of $[H^{\cdot}]$ and $[OH']$ can be altered by the admixture of *e.g.* alcohol in concentrations greater than normal, and probably also by salts in high concentration. This alteration will, however, hardly come into consideration in the majority of titration and physiological fluids.

*The Method of Electrical Conductivity.*

There is probably no physical property which has given a deeper insight into the nature of electrolytic equilibria than that of electrolytic conduction. The experimental methods established by Kohlrausch and the results obtained, have made it possible to find the concentrations of individual ions in solution and by difference also that of the uncharged molecules. The molecular conductance ($\Lambda$) is defined as the specific conductivity in reciprocal ohms ($\kappa$) per centimetre cube multiplied by the dilution in gram molecules per c.c.

If the dilution V is expressed in litres per mol, then

$$\Lambda = 1{,}000\ \kappa V.$$

In the case of strong electrolytes $\Lambda$ tends to a limit $\Lambda_0$ as V is increased indefinitely so that the electrolytic dissociation becomes complete. If $a$ = the degree of dissociation at a concentration at which the molecular conductivity $= \Lambda$

Then $$a = \Lambda/\Lambda_0.$$

The molecular conductivities $\Lambda$ and $\Lambda_0$ are equal to the sum of the conductivities of the anion $L_A$ and the kathion $L_K$. The value of $\Lambda_0$ for electrolytes which are only slightly dissociated at the highest experimental dilutions is determined indirectly by summing ${}_0L_A$ and ${}_0L_K$.

A determination of the conductivity at a standard temperature (18° or 25°) is therefore all that is required in order that the [H·] or [OH′] of an acid or base may be calculated, if ${}_0L_A$ and ${}_0L_K$ are known.

*Calculations of [H·] and [OH′] from conductivity and ionic mobility.*

Even if the exact nature of the acid or base is unknown, the degree of dissociation may be approximately calculated from the conductivity in view of the fact that this is chiefly due to the H· or OH′. The mobilities of organic anions and kathions are not only small compared to those of H· and OH′, but also do not differ much among themselves, if the members of each homologous series which have the lowest molecular weights are excluded.

| Anions at 25°. | Mobilities. |
|---|---|
| $CH_3 \cdot CH_2 \cdot COO'$ . . | 38 |
| $C_6H_5COO'$ . . . | 33 |
| $C_6H_4(CH_3)COO'$ . . | 30 |

| Kathions at 25°. | Mobilities. |
|---|---|
| $CH_3 \cdot CH_2 \cdot NH_3^{\cdot}$ . . | 50 |
| $C_6H_5 \cdot NH_3^{\cdot}$ . . . | 37 |
| $C_6H_4(CH_3)NH_3^{\cdot}$ . . | 36 |

From a mean value of 30 to 35 of the ionic mobilities at 25° together with the mobilities of $H^{\cdot}$ and $OH'$ given in the table, tbe concentrations of the latter may be approximately calculated from the conductivity of an unknown acid at 25°. The molar concentration of the acid or base must of course be known also, and the equations of p. 8 are applied.

The mobility of organic anions falls fairly regularly with the number of atoms after the first 12, and fairly accurate values of $\Lambda$ may be stated from the molecular weight irrespective of the nature of the acid by the use of the second table (Lunden).

| $t°$ = | 0 | 10 | 15 | 18 | 25 | 40 | 50 |
|---|---|---|---|---|---|---|---|
| $L_0$ of $H^{\cdot}$ = | 222 | 273 | 298 | 313 | 347 | 414 | 456 |
| $L_0$ of $OH'$ = | 118 | 149 | 165 | 174 | 196 | 224 | 276 |

| No. of Atoms in Acid. | $t$ = | 0 | 10 | 15 | 18 | 25 | 35 | 40 | 50 |
|---|---|---|---|---|---|---|---|---|---|
| 12 | $\Lambda_0$ of Acid = | 241 | 299 | 328 | 344 | 383 | 436 | 463 | 513 |
| 30 | $\Lambda_0$ of Acid = | 235 | 292 | 320 | 336 | 374 | 426 | 452 | 501 |

Values of $\Lambda_0$ may be interpolated. Thus the decrease is about one unit of $\Lambda$ for 3 atoms at 0°, one unit for $1\frac{1}{2}$ atoms at 50°.

*Calculation of* $[H^{\cdot}]$ *and* $[OH']$ *from dissociation constants.*

From the results of the conductivity measurements which have been made a series of tables could be drawn up

which would give the [H·] and [OH′] of all common acids and bases at all moderate and low concentrations.

When the acid or base is weak its dissociation may be expressed by a constant, and tables of [H·] and [OH′] may be constructed straightway from conductivity measurements. Thus for such electrolytes the dissociation may be expressed by a constant which is valid over a large range of concentrations C or volumes V.

If $a$ has the meaning given to it above, then

$$\frac{(aC)^2}{(1-a)\,C} = K\,\frac{a^2C}{1-a} \text{ or } \frac{a^2}{(1-a)\,V} = K$$

For an acid AH or a base BOH this equation may be written

$$\frac{[H\cdot]\,[A']}{[AH]} = K_A \quad . \quad . \quad . \quad (1a) \qquad \frac{[OH']\,[B\cdot]}{[BOH]} = K_B \quad . \quad (1b)$$

Since also $[H\cdot] = [A']$ $[OH'] = [B\cdot]$ and $C_A = [A'] + [AH]$ $C_B = [B\cdot] + [BOH]$ ($C_A$ and $C_B$ being the total concentrations of acid and base in any form of combination), equations (1$a$) and (1$b$) become—

$$\frac{[H\cdot]^2}{C-[H\cdot]} = K_A \quad . \quad . \quad . \quad (2a) \qquad \frac{[OH']^2}{C-[OH']} = K_B \quad . \quad (2b)$$

and

$$[H\cdot] = \frac{-K}{2} + \sqrt{\frac{K^2}{4} + KC} \quad . \quad (3a)$$

$$[OH'] = \frac{-K}{2} + \sqrt{\frac{K^2}{4} + KC} \quad . \quad (3b)$$

If now the degree of dissociation is less than 1%, [H·] or [OH′] in (2$a$) and (2$b$) may be neglected in comparison with C, and the equations are simplified to—

$$[H\cdot] \text{ or } [OH'] = \sqrt{KC} \quad . \quad (4a) \text{ and } (4b)$$

$$[H\cdot] = \frac{K_w}{\sqrt{K_B C}} \quad . \quad . \quad . \quad (4b)$$

The use of these simple equations is obvious. Thus, suppose it is required to find the concentration of acetic acid which will give about the same [H·] as a 0·001 N strong acid.

$$[H\cdot] = 1 \times 10^{-3} = \sqrt{KC} \text{ and } C = 0{\cdot}058 \text{ N.}$$

If the acids and bases are so weak that the [H·] and [OH′] of pure water are comparable with those which they produce, the equations need a slight modification. By the law of electrical neutrality (p. 3)

$$[H\cdot] = [A'] + [OH']$$

$$\therefore [H\cdot] = \frac{K_A C}{[H\cdot]} + \frac{K_W}{[H\cdot]} = \sqrt{K_A C + K_W}.$$

So also for a base

$$[OH'] = \sqrt{K_B C + K_W} \text{ or } [H\cdot] = \frac{K_W}{\sqrt{K_B C + K_W}}.$$

The very weakest acid cannot produce an [H·] nor the weakest base an [OH′] less than those concentrations which correspond to absolute neutrality. An acid of $K = 1 \times 10^{-14}$ if present in unit concentration will about double the normal [H·] of pure water.

These electrolytes may be most easily distinguished as acids or bases by the balanced neutrality which they produce in water. The [H·] of water containing a sugar or glycerine will not be diminished so rapidly by the addition of small quantities of alkali as will that of pure water.

*The Fractions ionised or not at a given Acidity.*

The equations on p. 11 may also be applied to finding the concentrations at which pure acids or bases are $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$, etc., dissociated. If it is desired also to calculate directly the amounts of undissociated acid, etc., the equations are best transformed so as to give $a$, etc. (the fraction dissociated) as a function of [H·] or K.

Thus $$\alpha = \frac{K}{K + [H^{\cdot}]} \text{ or } \frac{1}{1 + \frac{[H^{\cdot}]}{K}}$$

$$1 - \alpha = \frac{[H^{\cdot}]}{[H^{\cdot}] + K} \text{ or } \frac{1}{1 + \frac{K}{[H^{\cdot}]}}.$$

It is at once evident that weak acids and bases are one-half dissociated ($\alpha = 0{\cdot}5$) at $[H^{\cdot}] = K$ or $[OH'] = K$. Thus acetic acid must be present half as ion and half as uncharged molecule at $[H^{\cdot}] = 1{\cdot}8 \times 10^{-5}$, the corresponding state for ammonia occurring at $[OH'] = 1{\cdot}9 \times 10^{-5}$.

If the degrees of dissociation and the constants are given the extended meaning proposed by Michaelis,* then a certain ratio of ion fraction to ion residue $\alpha$ to $\rho$ always corresponds to a certain $[H^{\cdot}]$ no matter how this has been produced, except in so far as the presence of other compounds affects the value of K. Thus $\alpha$ for acetic acid may be reduced to a given value not only by increase of concentration in accordance with equation p. 11, but also by the addition of a strong acid. It may be increased not only by dilution but also by the addition of a strong base. Any process, physical or chemical, which alters $[H^{\cdot}]$ in the required ratio while not affecting K will have the same effect on $\alpha$. It is the almost complete dependence of many kinds of ionisations upon the concentrations of the hydrion and hydroxylion which has made it possible to sketch the outlines of a quantitative theory of indicators.

*The Determination of the Acidity due to a Mixture of Acids.*

There are three principal cases :—

(1) The constants of the two acids are equal. The

* Ion fraction $\alpha$ = ion/total acid in any form. Ion residue $\rho$ = undissociated acid/total acid in any form.

hydrion concentration may then be calculated as if the total concentration of a single acid were equal to $C_1 + C_2$.

(2) The acids are strong, and neither has a dissociation constant. Since the hydrion concentrations of strong acids are nearly the same at corresponding concentrations, that of the mixture will often be approximately equal to that of either acid at concentration $C = C_1 + C_2$.

(3) The two acids have dissociation constants which differ from one another. If the constants are $K_1$ and $K_2$ and the concentrations $C_1$ and $C_2$, then it has been shown (Abegg Ahrens' Sammlung VIII., 1903) that the ratio of the degree of dissociation $\beta_1$ of acid 1 before mixing to that $\alpha_1$ after mixing with $C_2$ of 2 is given by the equation—

$$\frac{\beta_1}{\alpha_1} = \sqrt{1 + \frac{K_2 C_2}{K_1 C_1}}$$ and similarly for acid 2,

$$\frac{\beta_2}{\alpha_2} = \sqrt{1 + \frac{K_1 C_1}{K_2 C_2}}$$

The $[H^{\cdot}]$ of such a mixture may be obtained directly from the equation—

$$[H^{\cdot}] = \sqrt{K_1 C_1 + K_2 C_2}$$

(It is understood that $\alpha_1$ and $\alpha_2$ are such that $1 - \alpha_1$ and $1 - \alpha_2$ are approximately equal to 1).

If $$C_1 = C_2 = \frac{C}{2}$$

$$[H^{\cdot}] = \sqrt{\frac{(K_1 + K_2)\, C}{2}},$$

or the mixture of acids behaves as one present at the concentration C and having the mean dissociation constant of the two. The hydrion concentration will be intermediate between that given by the stronger and that given by the weaker at the concentration $\frac{C}{2}$, but will evidently be nearer

to the former than to the latter. The weaker acid affects the ionisation of the stronger little, the stronger that of the weaker much. This fact is used in detecting the presence of a strong acid in a weaker one.

*Dissociation Constants.*

The selected lists of dissociation constants given below are founded on the results of Walker and his co-workers from 1900 onwards in the *J. Chem. Soc.* and *Zeitsch. f. phys. Chem.:* W. Ostwald, *Zeitsch. f. phys. Chem.*, 1888 and 1889 (organic acids); Bredig, *Zeitsch. phys. Chem.*, 13, 289 (1894) (organic bases); Hantzsch and Sebaldt, *Zeitsch. phys. Chem.*, 30, 258 (1899).

The collection made by Lunden Ahrens' Sammlung XIV. has also been much used.

These results, founded mainly on the conductivities of the acids and bases and their hydrolysed salts have been in many cases confirmed by the hydrogen electrode (see phosphoric, boric acid, etc., p. 270), or by the colorimetric method (Veley, J., *Chem. Soc.* (1907—1909); Salm, *Zeitsch. phys. Chem.*, 63, 83 (1908)); or by the velocity method, especially by the velocity of inversion of cane sugar (Smith, *Zeitsch. phys. Chem.*, 25, 193 (1898)); or by partition ratio (Wegscheider *Zeitsch. Elektrochem.*, 14, 740 (1908); B. de Szyszkowski, p. 26).

When the results of different experimenters using different methods are compared together, the agreement is in most cases fair, but not so close as to allow mean values to be stated say for each 5° within the ordinary range of temperature. The mean values of the constants tabulated below must therefore be taken as approximately correct for temperatures from 15° to 25°, and in many cases from 0° to 25°. For a fuller account of individual values of the con-

stants, together with a complete bibliography, the reader is referred to "The Electrical Conductivity and Ionisation Constants of Organic Compounds," by Heyward Scudder, B.A., B.S., M.D. (Constable & Company, 1914).

From the constants, the $[H^{\cdot}]$ and $[OH']$ of the pure acids and bases at each concentration are obtained from equations, p. 11.

The $[H^{\cdot}]$, due to the first dissociation of di- and poly-hydrion acids, is calculated in precisely the same way, up to the dilution at which the second dissociation begins to be appreciable.

The $[H^{\cdot}]$ and $[OH']$ due to the hydrolysis of salts are calculated according to pp. 30, 31, 32.

*Very Weak Acids.*

| Name and Formula. | Values of K. | Approximate mean K. |
|---|---|---|
| Glycerol ($C_3H_5(OH)_3$) | $7 \times 10^{-15}$ | |
| Cane-sugar, sucrose, saccharose ($C_{12}H_{22}O_{11}$) | $2{\cdot}4 \times 10^{-13}$ | |
| Glucose, dextrose ($C_6H_{12}O_6$) | $6 \times 10^{-13}$ | |
| Hydrogen peroxide ($H_2O_2$) | $2 \times 10^{-12}$ | |
| Carbolic acid, phenol ($C_6H_5OH$) | $5{\cdot}8 \times 10^{-11} - 1{\cdot}3 \times 10^{-10}$ | $1 \times 10^{-10}$ |
| Hydrocyanic acid (HCN) | $4{\cdot}7 \times 10^{-10} - 1{\cdot}3 \times 10^{-9}$ | $1 \times 10^{-9}$ |
| Hypochlorous (HOCl) | $4 \times 10^{-8}$ | |
| Hydrogen sulphide ($H_2S$) | $5{\cdot}7 \times 10^{-8}$ | |

*Weak and Moderately Strong Acids.*

| Name and Formula. | Values of K. | Approximate mean K. |
|---|---|---|
| Uric ($C_5H_4O_3N_4$) . . | $1{\cdot}5 \times 10^{-6}$ | |
| Acetic ($CH_3COOH$) . . | $1{\cdot}78 - 1{\cdot}85 \times 10^{-5}$ | $1{\cdot}8 \times 10^{-5}$ |
| Propionic ($C_2H_5COOH$) . | $1{\cdot}3 - 1{\cdot}4 \times 10^{-5}$ | |
| Benzoic ($C_6H_5COOH$) . | $6 - 7{\cdot}3 \times 10^{-5}$ | $7 \times 10^{-5}$ |
| Glycollic ($CH_2OH{\cdot}COOH$) | $1{\cdot}5 - 1{\cdot}57 \times 10^{-4}$ | $1{\cdot}5 \times 10^{-4}$ |
| Lactic ($CH_3{\cdot}CHOH{\cdot}COOH$) | $1{\cdot}4 \times 10^{-4}$ | |
| Formic ($HCOOH$) . . | $2{\cdot}07 - 2{\cdot}14 \times 10^{-4}$ | $2 \times 10^{-4}$ |
| Nitrous ($HNO_2$) . . | $4 - 6 \times 10^{-4}$ | $5 \times 10^{-4}$ |
| Salicylic ($C_6H_4(OH)COOH$) | $0{\cdot}8 - 1{\cdot}1 \times 10^{-3}$ | $1 \times 10^{-3}$ |

*Variation in Dissociation Constants with Dilution.*

*Acetic Acid at 25°.*

| | | | | | | |
|---|---|---|---|---|---|---|
| C = | 2·744 | 2·000 | 1·405 | 0·9412 | 0·4565 | 0·2941 |
| $K \times 10^5$ = | 0·81 | 1·07 | 1·31 | 1·52 | 1·67 | 1·77 |

| | | | | |
|---|---|---|---|---|
| C = | 0·2107 | 0·0429 | 0·0313 | 0·00926 |
| $K \times 10^5$ = | 1·79 | 1·85 | 1·89 | 1·90 |

(Rivett and Sidgwick, *J. Chem. Soc.*, 97, i., 736 (1910).)

*Inactive Butyric Acid.*

| | | | | | |
|---|---|---|---|---|---|
| $v$ = | 2 | 8 | 32 | 128 | 1024 |
| $K \times 10^5$ = | 1·08 | 1·47 | 1·48 | 1·49 | 1·47 |

*Propionic Acid.*

| | | | | | |
|---|---|---|---|---|---|
| $v$ = | 2 | 8 | 32 | 128 | 1024 |
| $K \times 10^5$ = | 1·16 | 1·38 | 1·41 | 1·38 | 1·32 |

*Electrical Conductivities.* (H. C. Jones.)

*Malonic Acid.*

| | | | | | |
|---|---|---|---|---|---|
| $v$ = | 2 | 8 | 32 | 128 | 1024 |
| $K \times 10^5$ = | 161 | 164 | 163 | 164 | 167 |

*Cyanacetic Acid.*

| | | | | |
|---|---|---|---|---|
| $v =$ | 16·82 | 33·64 | 67·28 | 125 |
| $K \times 10^5 =$ | 402 | 392 | 383 | 378 |

(Kendall, *J. Chem. Soc.*, 101, 1275 (1912).)

*Stronger Acids, for which Constants can be Formulated.*

| Name and Formula. | Values of K. | Approximate mean K. |
|---|---|---|
| Chloracetic ($CH_2Cl \cdot COOH$) | $1{\cdot}55 - 1{\cdot}8 \times 10^{-3}$ | $1{\cdot}6 \times 10^{-3}$ |
| Dichloracetic ($CHCl_2 \cdot COOH$) | $5{\cdot}14 - 6{\cdot}3 \times 10^{-2}$ | $5{\cdot}1 \times 10^{-2}$ |
| Trichloracetic ($CCl_3COOH$) | 2 — 4 | 3 |
| Picric acid . . . 2, 4, 6 trinitrophenol ($C_6H_2(OH)(NO_2)_3$) | 1·6 — 2·3 | 2 |

*Bases.*

| Name and Formula. | Values of K. | Approximate mean K. |
|---|---|---|
| Acetamide ($CH_3CONH_2$) . | $3{\cdot}1 \times 10^{-15}$ | |
| Urea ($CO(NH_2)_2$) . . | $0{\cdot}67 - 3{\cdot}4 \times 10^{-14}$ | $1{\cdot}5 \times 10^{-14}$ |
| Aniline ($C_6H_5(NH_2)$ . | $2{\cdot}6 - 5 \times 10^{-10}$ | $3{\cdot}5 \times 10^{-10}$ |
| p. toluidine ($C_6H_5(CH_3)NH_2$) | $0{\cdot}45 - 3{\cdot}6 \times 10^{-9}$ | $1{\cdot}6 \times 10^{-9}$ |
| Pyridine ($C_5H_5N$) . . | $1{\cdot}06 - 3 \times 10^{-9}$ | $1{\cdot}6 \times 10^{-9}$ |
| Hydrazine ($N_2H_4$) . . | $2 \times 10^{-6}$ | |
| Ammonia ($NH_3$) . . | $1{\cdot}35 - 4 \times 10^{-5}$ (see also p. 56) | $1{\cdot}8 \times 10^{-5}$ |
| Methylamine ($NH_2 \cdot CH_3$) | $4 \times 10^{-4}$ | |
| Dimethylamine ($NH(CH_3)_2$) | $5 - 6 \times 10^{-4}$ | $5{\cdot}5 \times 10^{-4}$ |
| Trimethylamine ($N(CH_3)_3$) | $6 - 7 \times 10^{-5}$ | $6{\cdot}5 \times 10^{-5}$ |
| Quinine ($C_{20}H_{24}O_2N_2$) - | $K_1 = 26 - 120 \times 10^{-7}$<br>$K_2 = 1{\cdot}3 - 3{\cdot}3 \times 10^{-7}$ | |
| Nicotine ($C_{10}H_{14}N_2$) . | $0{\cdot}3 - 3 \times 10^{-5}$ | |

*Amphoteric Compounds.*

| Name and Formula. | Values of K. | Approximate mean K. |
|---|---|---|
| Glycine or amido acetic acid $(CH_2(NH_2)\cdot COOH)$ | $K_A = 1\cdot7 - 3\cdot4 \times 10^{-10}$<br>$K_B = 2\cdot7 \times 10^{-12}$ | |
| Arsenious acid $(As(OH)_3)$ | $K_A = 6 \times 10^{-10}$<br>$K_B = 1 \times 10^{-14}$ | |
| Cacodylic acid $((CH_3)_2\ AsO \cdot OH)$ | $K_A = 6\cdot4 - 7\cdot5 \times 10^{-7}$<br>$K_B = 3\cdot8 - 5\cdot6 \times 10^{-13}$ | $7 \times 10^{-7}$<br>$5 \times 10^{-13}$ |

*Acids which give more than one [H·]. Bases which give more than one [OH′].*

The hydrion and hydroxylion concentrations in solutions of acids and bases which are capable of giving more than one [H·] or [OH′] from each molecule are probably governed by the same kinds of equilibria already discussed. Thus the ionisations of $H_2SO_4$ are those of a strong acid, and neither the first nor the second can be expressed by a dissociation constant. Where constants can be defined those after the first are best investigated by means of the conductivity, catalytic effect, etc., of the acid salt, or generally from the neutralisation curve (Chap. VI.). The calculation of [H·] or [OH′] in solutions of the free acids or bases is somewhat simplified by the fact that one dissociation constant suffices down to concentrations of about 0·002N, or those at which the dissociation of one H· has proceeded to the extent of about 50 per cent. Down to this hydrion concentration or that at which [H·] = $K_1$ (see equation, p. 13), the acid behaves as monobasic with a constant $K_1$. This constant $K_1$ has not quite the same meaning as that of a monobasic

acid, for the first dissociation may take place in two ways. Thus if the residue of the one kind of dissociation is denoted by $A_1$, that of the other kind by $A_2$, and that of both together by A—

$$[H\cdot]\,[HA_1'] = K_1 HAH$$

$$[H\cdot]\,[HA_2'] = K_2 HAH$$

and

$$\frac{[H\cdot]\,([HA_1'] + [HA_2'])}{HAH} = K_1 + K_2.$$

The observed $K_1$ is the sum of two theoretical constants which would be characteristic of the first and second dissociation if they could be observed separately. The theory here supplies a reason, why comparing monobasic with dibasic acids of similar structure, the latter should be the stronger. A further reason is the increased electronegative character which is given to either anion by the presence of the other COOH group.

Thus for succinic acid (·COOH) $C_2H_4$(.COOH) $K_1 = 6{\cdot}7 \times 10^{-5}$ and for butyric acid (·$CH_3$) $C_2H_4$ (COOH) $K = 1{\cdot}5 \times 10^{-5}$. The strengthening due to the other ·COOH group is naturally more marked in the case of propionic and malonic acids, for the COOH groups are nearer together in this case.

When the first dissociation has taken place in either way, the second in most cases takes place to a much smaller extent, and the higher the first constant (*i.e.*, the practical constant actually observed $= K_1 + K_2$ above), the lower is the second as a rule. Apparently the presence of one negative electron on the molecule makes the assumption of a second more difficult.

Thus the ratio between $K_1$ and $K_2$ for succinic acid is 25, while the same ratio for oxalic acid with a higher $K_1$ is 780 (see tables, next page).

*Constants of Di- and Polybasic Acids.*

| Acid. | $K_1$ | K |
|---|---|---|
| Oxalic (COOH · COOH) | 0·1 to 0·04<br>0·7 | 1·6 to 4·9 × $10^{-5}$<br>3 × $10^{-5}$ |
| Citric . . . | 8 × $10^{-4}$ | 3·2 × $10^{-5}$<br>$K_3$ = 7 × $10^{-7}$ |
| Sulphurous ($H_2SO_3$) | 1·64 to 1·74 × $10^{-2}$<br>1·7 × $10^{-2}$ | 5 × $10^{-6}$ |

*Constants of Di- and Polybasic Acids.*
(See also Chap. VII. for Phosphoric, etc.)

| Acid. | Individual Values of $K_1$ and Approximate Mean Value. | Values of $K_2$. |
|---|---|---|
| Malic (COOH · CHOH · $CH_2$ · COOH) | 4 × $10^{-4}$ | 7·5 × $10^{-6}$ |
| Tartaric (COOH · CHOH · CHOH · COOH) | 5 to 11 × $10^{-4}$<br>1 × $10^{-3}$ | 3·4 to 5·9 × $10^{-5}$<br>5 × $10^{-5}$ |
| Succinic (COOH · $CH_2$ · $CH_2$ · COOH) | 6·35 to 6·9 × $14^{-5}$<br>6·5 × $10^{-5}$ | 2·2 to 4 × $10^{-6}$<br>3 × $10^{-6}$ |
| Fumaric (COOH · CH : CH · COOH) . | 9·4 × $10^{-4}$ to 1·1 × $10^{-3}$<br>1 × $10^{-3}$ | 1·8 to 3·2 × $10^{-5}$<br>2·5 × $10^{-5}$ |
| Maleic (COOH · CH : CH · COOH) . | 1·2 to 1·4 × $10^{-2}$<br>1·3 × $10^{-2}$ | 2·0 to 3·9 × $10^{-7}$<br>3·0 × $10^{-7}$ |
| Malonic (COOH · CH · COOH) . . | 1·5 to 1·7 × $10^{-3}$<br>1·6 × $10^{-3}$ | 1 to 2·1 × $10^{-6}$<br>1·5 × $10^{-6}$ |

*Deviations from the Dilution Law.*

Although the dissociation constants suffice for the approximate determination of [H·] and [OH'] over a wide range, yet there is no case in which the constant holds good at all dilutions.

The deviations fall into two extreme classes:—

(*a*) Weak electrolytes.

(*c*) Strong electrolytes.

Between these lies the class of

(*b*) Transition electrolytes.

(*a*) It has been shown by Wegscheider, *Zeitsch. phys. Chem.*, 69, 603 (1909), that the constants of weak electrolytes begin to decrease above a certain concentration and usually between V = 16 and V = 32 (C = 0·06 and 0·03). For acids of this class there may be a maximum of K at a dilution slightly greater than that at which K decreases. For examples of this variation see p. 17. The positive or negative variation in constants of the order $1 \times 10^{-3}$ is very slight (see Malonic Acid, p. 17).

(*b*) The class of transition electrolytes with constants between 0·001 and 0·01 range from a very slight to an almost complete ionisation at the highest dilutions at which measurements can be made (Kendall, *J. Chem. Soc.*, 101, 1275 (1912)). The dissociation constants show the opposite effect to that of class (*a*), *i.e.*, they begin to increase above a certain concentration (see Cyanacetic Acid, p. 18). The higher the dissociation constant the lower is the concentration at which the rapid increase begins. Thus this concentration corresponds to V = 256 for nitrobenzoic acid, $K = 633 \times 10^{-5}$. There are many moderately strong acids, however, *e.g.*, formic and trichloracetic, which obey the dilution law up to higher concentrations. Apart from these exceptions it appears that the above generalisation, connecting the magnitude of dissociation constants with the concentrations at which the increase or decrease takes place, will account for the facts in a qualitative manner. It has been greatly extended by Arrhenius and successfully applied by him to explain the anomaly of strong electrolytes.

(*c*) In the case of highly dissociated acids, bases and salts the ionisation "constant" increases rapidly with increase of concentration.

Thus, according to Bancroft, *Zeitsch. phys. Chem.*, 31, 188

(1898), the "constant" for HCl increases from 3·42 at V = 1,000 to 4·58 at V = 50, and afterwards decreases to 0·23 in 10 normal solutions.

The two directions of change, that characteristic of strong electrolytes * and that characteristic of highly concentrated solutions † are clearly marked in the case of HCl and KOH.

| | | | | | | |
|---|---|---|---|---|---|---|
| HCl | V = | 2 | 1 | $\frac{1}{2}$ | $\frac{1}{8}$ | $\frac{1}{5}$ | $\frac{1}{10}$ |
| | K = | 2·68 | †3·04 | 2·71 | *2·22 | 1·34 | 0·35 |
| KOH | V = | 2 | 1 | $\frac{1}{2}$ | $\frac{1}{8}$ | $\frac{1}{5}$ | $\frac{1}{10}$ |
| | K = | 1·95 | †2·59 | 2·78 | *2·53 | 1·76 | — |

(Wegscheider, ref. p. 22).

*Ionisation in Concentrated Solutions.*

A consideration of all the methods of determining [H·] and the result of the application of these to more concentrated solutions make it evident that the regularities of dilute solutions cease to hold good. The correction of these deviations by the introduction of more or less empirical functions can only be touched upon here. That which would have the clearest physical meaning would be a correction for viscosity. Unfortunately, however, there is no one form of a viscosity function which will equally regularise the anomalies of different electrolytes. Thus, although the simple multiplication of $\Lambda$ values by $\eta$ = the relative viscosity (water = 1) at the given concentration does improve the constant of acetic acid up to C = 0·95 (Rivett, *J. Chem. Soc.*, 97, 736 (1910)), yet, in some cases, as with sodium acetate, such a correction appears to make the ionisation increase with increasing concentration. If it is necessary to introduce a different power of $\eta$ for each electrolyte then the correction loses its theoretical significance, and the viscosity as a factor may well be left out of consideration and replaced by the most convenient empirical formula available. It appears advisable at present to use the simple equations of chemical

equilibrium as far as possible, recognising them as limiting laws with a considerable range of utility, but in strong solutions masked by interactions between the molecules (especially perhaps variable degrees of hydration) which profoundly modify the ionising power, etc., of the solvent. At present it seems best to deduce the [H·] and [OH′] of concentrated solutions from the experimental data in the manner accepted for diluted solutions.

*Formulæ for Strong Electrolytes.*

The problem of finding an empirical constant which shall represent the ionisation of highly dissociated electrolytes also was undertaken with partial success by Rudolphi (*Zeitsch. phys. Chem.*, 17, 385 (1895)), and Van't Hoff and Kohlrausch (*Zeitsch. phys. Chem.*, 18, 301, 662 (1895)).*

The function $\frac{a^3C}{(1-a)^2} = K$ or $\frac{i^3}{u^2} = K$

(in which "$i$" stands for the concentration of ion, "$u$" for that of undissociated molecule) varies from 4·41 at V = 2 to 5·29 at V = 32 in the case of HCl. With other electrolytes a greater constancy is often found. As a matter of fact the exponent of $i$, assumed to be 1·5 in the above equation which is equivalent to

$$\frac{i^{1.5}}{u} = K,$$

varies with different electrolytes from 1·4 to 1·577 (Storch, *Zeitsch. phys. Chem.*, 19, 13 (1896)).

The abnormality may be referred either to the ions or to the molecules.

If the former, the equation takes the form given above, or

$$\frac{i^2}{u} = K\sqrt{i}$$ (Arrhenius),

* See also Ahrens' Sammlung Bd. 8 Heft 5 to 7; Bd. 10 Die Anomalie der Starken Electrolyte, Drucker, 1905.

or introducing the exponent "$n$" instead of 1·5

$$\frac{i^n}{u} = K \qquad \frac{i^2}{u} = Ki^{2-n}.$$

If it is the molecules which do not react according to their concentration, a view for which independent evidence has been brought forward by Walker (*Brit. Assoc. Reports*, 1911, p. 349), then the equations must be written:—

$$\frac{i^2}{u^{\frac{3}{2}}} = K \qquad \frac{i^2}{u} = K\sqrt[3]{u} \qquad \frac{i^2}{u} = Ku^{\frac{2}{n}-1}.$$

Since no value of $n$ expresses the facts perfectly, it appears that the want of agreement between the true and the effective concentrations depends upon other factors than those in the equations. These may be used, however, for dilute solutions. Thus for HCl and KOH the exponents $n$ have the average value of 1·4 up to a concentration of about 0·001; beyond this they gradually increase, but decrease again from $c = 0{\cdot}02$.

According to the hypothesis of Arrhenius (*Zeitsch. phys. Chem.* 31, 188 (1898)), the deviations from the law of mass action must be referred both to ions and to molecules. The constant should contain a function either of the former or of the latter according to circumstances. Any great increase in the concentration of the solute alters the nature of the solvent. The interaction of the molecules of the solute with one another is affected not merely by the total volume, but also by the attractive force of the molecules of solute and solvent. It is the constancy of the latter effect in dilute solutions which allows the mass action equations to be verified at all. With increasing concentration the attractive forces change their nature and the system comes to resemble in one sense a highly compressed gas in which also the deviations from the gas laws must be expressed by empirical constant. Since an increase in the concentration

of a strong electrolyte increases chiefly the concentration of the ions, while in the case of a weak electrolyte it increases the concentration of the uncharged molecules, it may be supposed that increase of ionic concentration has a raising effect, but increase of molecular concentration a lowering effect, upon the constant.

This generalisation accounts in a qualitative manner for the alteration of the dissociation constants of both weak and strong electrolytes.

According to Wegscheider (ref., p. 22) the dilution law only holds for medium strong acids when the ionic concentration is less than N/60, or for binary electrolytes in general if $2V/a$ is less than 120.

Kendall* finds that $2V/a$ must be less than 600 in the case of acids mentioned on p. 17. He introduces a correction in the form $\frac{a^2}{(1-a)V} = K + c\left(\frac{1-a}{a}\right)$ in which $c$ is a constant small for weak electrolytes and large for strong electrolytes. For further correction factors containing ionic concentrations and discussion of the subject generally, see Kraus and Bray, *J. Amer. Chem. Soc.* 35, 1315 (1913); Arrhenius, *Medd. K. Vetensk. Nobelinstitut.* 2, 42 (1913); de Szyszkowsky, *ibid.*, 2, 41 (1913).

A few tables of [H·] and [OH′] as calculated from the conductivity are given in the following pages. For other values which have been used as standards, see Chap. V.

*Hydrochloric Acid at* 18° (Kohlrausch).

| | | | | | | |
|---|---|---|---|---|---|---|
| C = | 0·001 | 0·002 | 0·005 | 0·01 | 0·02 | 0·03 |
| 100$a$ = | 98·2 | 98·0 | 97·3 | 96·4 | 95·7 | 94·9 |
| C = | 0·05 | 0·10 | 0·20 | 0·30 | 0·50 | 1·0 |
| 100$a$ = | 93·8 | 91·4 | 89·1 | 87·5 | 85·3 | 78·5 |
| C = | 2·0 | 3·0 | 4·0 | 5·0 | 7·15 | 10·0 |
| 100$a$ = | 66·2 | 56·0 | 47·3 | 39·6 | 27·7 | 16·8 |

* *J. Chem. Soc.* 101, 1275 (1912).

Empirical constant—

$$\frac{(aC)^{1\cdot4}}{(1-a)C} = 4\cdot1 \text{ up to } C = 0\cdot5.$$

*Nitric Acid at* 18° (Noyes, Melcher, Cooper and Eastman, *Zeitsch. phys. Chem.*, 70, 364 (1910)).

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $C =$ | $0\cdot0_35$ | 0·002 | 0·01 | 0·0125 | 0·05 | 0·08 | 0·10 |
| $[H^{\cdot}] =$ | $0\cdot0_349_5$ | $0\cdot0019_7$ | 0·0097 | 0·0121 | 0·047 | 0·074 | 0·092 |

*Nitric Acid at* 100°.

*Ibid.* (same concentrations).

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $[H^{\cdot}] =$ | $0\cdot0_349_3$ | $0\cdot0019_5$ | 0·0095 | 0118 | 0·045 | 0·071 | 0·088 |

*Sulphuric Acid at* 18° (Noyes, *ibid.*).

| | | | | |
|---|---|---|---|---|
| C (equivalents) = | 0·0002 | 0·0005 | 0·002 | 0·01 |
| (H.) mean = | $0\cdot0_3195$ | $0\cdot0_349$ | $0\cdot0018_5$ | $0\cdot0825_5$ |
| C (equivalents) = | 0·0125 | 0·05 | 0·08 | 0·10 |
| (H.) mean = | 0·01 | 0·034 | 0·053 | ·063 |

The degrees of dissociation may be calculated on the assumption (1) that $H^{\cdot}$ and $SO_4''$ ions alone are formed, (2) that $H^{\cdot}$ and $HSO_4'$ alone are formed. The values given are the mean of (1) and (2).

*Sulphuric Acid at* 100°.

| | | | | |
|---|---|---|---|---|
| C (equivalents) = | 0·002 | 0·010 | 0·050 | 0·10 |
| $[H^{\cdot}]$ = | 0·00136 | 0·0056 | 0·0245 | 0·048 |

*Potassium Hydrogen Sulphate at* 18°.

| | | | | |
|---|---|---|---|---|
| C (mols.) = | 0·002 | 0·01 | 0·05 | 0·10 |
| $[H^{\cdot}]$ = | 0·00178 | 0·0074 | 0·028 | 0·051 |

*Potassium Hydrogen Sulphate at* 100°.

| | | | | |
|---|---|---|---|---|
| C (mols.) = | 0·002 | 0·01 | 0·05 | 0·10 |
| $[H^{\cdot}]$ = | 0·001 | 0·0031 | 0·008 | 0·014 |

*Orthophosphoric Acid at* 18° (Noyes).

| C (mols.) = | $0{\cdot}0_32$ | $0{\cdot}0_22$ | 0·01 | 0·0125 | 0·05 | 0·08 | 0·10 |
|---|---|---|---|---|---|---|---|
| $100a$ = | 98 | 84 | 60 | 56·5 | 36·5 | 31·0 | 28·5 |

*Orthophosphoric Acid at* 100° (Noyes).

| $100a$ = | 94·5 | 68·5 | 42·0 | 39·0 | 23·0 | 19·5 | 17·5 |
|---|---|---|---|---|---|---|---|

*Hydrofluoric Acid* probably ionises into H· and $HF_2'$ It begins to show the anomaly of strong electrolytes at about V = 128 (Wegscheider).

| V = | 4 | 8 | 16 | 32 | 64 | 128 | 256 | 512 | 1024 |
|---|---|---|---|---|---|---|---|---|---|
| $100a$ = | 7·4 | 9·0 | 11·1 | 14·9 | 19·7 | 26·2 | 37·6 | 44·4 | 56·1 |

Average ionisation of strong monobasic acids HX (Noyes and Falk, *J. Amer. Chem. Soc.*).

| C = | 0·001 | 0·002 | 0·005 | 0·01 | 0·02 | 0·05 | 0·10 |
|---|---|---|---|---|---|---|---|
| $100a$ = | 99·1 | 98·8 | 98·1 | 97·1 | 96·2 | 94·2 | 92·3 |

*Sodium Hydroxide at* 18° (Noyes).

| C = | 0·002 | 0·004 | 0·01 | 0·02 | 0·05 |
|---|---|---|---|---|---|
| [OH′] = | 0·00186 | 0·0039 | 0·0096 | 0·019 | 0·046 |

*Sodium Hydroxide at* 100° (same concentrations).

| [OH′] = | 0·00186 | 0·0039 | 0·0096 | $0{\cdot}018_8$ | $0{\cdot}045_5$ |
|---|---|---|---|---|---|

*Sodium Hydroxide* (Kohlrausch).

| C = | 0·005 | 0·01 | 0·05 | 0·10 |
|---|---|---|---|---|
| [OH′] = | 0·048 | 0·0095 | 0·046 | 0·088. |

*Barium Hydroxide at* 18°.

| C (equivalents) = | 0·0005 | 0·002 | 0·01 | 0·0125 |
|---|---|---|---|---|
| [OH′] = | 0·00049 | 0·0018 | 0·0093 | 0·0115 |
| C (equivalents) = | 0·05 | 0·08 | 0·10 | |
| [OH′] = | 0·043 | 0·066 | 0·081 | |

*Barium Hydroxide at* 100° (same concentrations).

[OH′] = 0·00049 $0{\cdot}0018_2$ 0·0091 0·0104 0·037 0·056 0·068.

*Potassium Hydroxide at* 18° (Kohlrausch).

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C = | 0·001 | 0·002 | 0·005 | 0·01 | 0·02 | 0·03 | 0·04 |
| $100a$ = | 97·7 | 96·8 | 96·2 | 95·3 | 94·9 | 92·7 | 91·4 |
| C = | 0·10 | 0·20 | 0·30 | 0·50 | 1·0 | | |
| $100a$ = | 88·9 | 86·1 | 84·9 | 82·2 | 76·9 | | |
| C = | 2·0 | 3·0 | 4·0 | 5·0 | 7·15 | 10·0 | |
| $100a$ = | 67·2 | 58·8 | 51·1 | 44·2 | 32·3 | 18·7 | |

Empirical constant $\dfrac{(aC)^{1\cdot4}}{(1-a)\,C} = 3\cdot05.$

*Sodium Hydroxide at* 18° (Kohlrausch).

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C = | 1·0 | 2 | 3 | 4 | 5 | 7 | 10 |
| $100a$ = | 73·3 | 60·1 | 49·5 | 39·7 | 31·6 | 20·0 | 9·28 |

*Hydrolysis.*

The acid or alkaline reaction of solutions of chemically neutral salts, such as $FeCl_3$, KCN, $Na_2CO_3$, $NH_4Cl$, is quantitatively related to the dissociation constants of the weak acid or alkali. If the dissociation constants $K_A$ or $K_B$ are very low then even the [H·] or [OH′] of pure water may require a considerable concentration of undissociated acid or base. A rearrangement must then take place so that the [H·] or [OH′] is diminished and [HA] or [BOH] is increased. In the first case OH′ ions take the place of A′ ions, so that the dissociated strong base is formed instead of the salt; in the second case dissociated strong acid is formed. Thus a solution of KCN contains free alkali and smells of HCN, while a solution of $NH_4Cl$ contains free acid and loses on boiling $NH_3$, which is produced by the dehydration of $NH_4OH$.

The quantitative relations are expressed by equations (1) to (4), p. 30.

If (2) is multiplied by (3) and $K_W$ is substituted for [H·]

[OH′], an equation is obtained which gives the constant of hydrolysis $K_h$.

$$\frac{[BOH]\,[AH]}{[A']\,[B\cdot]} = \frac{K_W}{K_A \cdot K_B} = K_h \quad . \quad . \quad (1)$$

or $$\frac{[\text{base}] \times [\text{acid}]}{[\text{salt}]^2} = \text{constant.}$$

Equations of this form must be used when both acid and base are weak. If the base is strong and the acid weak, equation (1) by substitution for $K_B$ is converted into (2*a*); while if the base is weak and the acid strong it is converted into (2*b*).

$$\frac{[OH']\,[AH]}{[A']} = \frac{K_W}{K_A} \quad . \quad . \quad . \quad (2a)$$

$$\frac{[H\cdot]\,[BOH]}{[B\cdot]} = \frac{K_W}{K_B} \quad . \quad . \quad . \quad (2b)$$

The degree of hydrolysis "$h$" may be defined as the total amount of acid or base (ionised or not) formed from one equivalent of the salt. The total concentrations of acid or base are $h$ C, where C is the total concentration and that of the unhydrolysed salt is $(1 - h)$ C.

Writing $a_A$, $a_B$, $a_S$ for the degrees of ionisation of acid-base and salt, equation (2*a*) becomes—

$$\frac{a_B\,(1 - a_A)\,h^2C^2}{a_S\,(1 - h)\,C} = \frac{K_W}{K_A} \quad . \quad . \quad . \quad (3a)$$

and equation (2*b*) becomes

$$\frac{a_A\,(1 - a_B)\,h^2C^2}{a_S\,(1 - h)\,C} = \frac{K_W}{K_B} \quad . \quad . \quad . \quad (3b)$$

$$\text{or } K_h = \frac{h^2C}{1 - h} = \frac{a_S}{a_B(1 - a_A)}\frac{K_W}{K_A} \quad . \quad . \quad (4a)$$

$$= \frac{h^2C}{1 - h} = \frac{a_S}{a_A\,(1 - a_B)}\frac{K_W}{K_B} \quad . \quad . \quad (4b)$$

For very large degrees of hydrolysis or in concentrated solutions the above general equations must be used in full.

If the degree of hydrolysis is low, some simplifications may be introduced. If $K_A$ or $K_B$ are not less than $1 \times 10^{-8}$ and the total concentration not less than about 0·01, then $1 - h$ is practically equal to 1. If the concentration is not too high; $a_S$, $a_B$, $1 - a_A$ of equation (4*a*) $a_S$, $a_A$, $1 - a_B$ of (4*b*) may also be taken as 1.

The degree of hydrolysis may then be very simply calculated.

$$h = \sqrt{\frac{K_W}{K_A C}} \quad . \quad . \quad . \quad . \quad (5a)$$

$$h = \sqrt{\frac{K_W}{K_B C}} \quad . \quad . \quad . \quad . \quad (5b)$$

The values of [OH′] and [H·] = $h$C may also be approximately calculated.

$$[OH'] = \sqrt{\frac{K_W C}{K_A}} \quad . \quad . \quad . \quad (6a)$$

$$[H\cdot] = \sqrt{\frac{K_W C}{K_B}} \quad . \quad . \quad . \quad (6b)$$

If the total concentrations are higher and it is desired to include the values of $a_A$, etc., the values of [H·] and [OH′] may be obtained by substitution in (2*a*) and (2*b*).

For

$$[AH] = \frac{[OH']}{a_B} \text{ and } BOH = \frac{[H\cdot]}{a_A}.$$

Hence

$$[OH']^2 = a_B a_S \frac{K_W C}{K_A} \quad . \quad . \quad . \quad (7a)$$

and

$$[H\cdot]^2 = a_A a_S \frac{K_W C}{K_B} \quad . \quad . \quad . \quad (7b)$$

For calculating a very low degree of hydrolysis, Bjerrum

"Die Theorie der alk. u. azid. Titrierungen," Ahrens' Sammlung (W. Herz), 21, 13, has proposed the formula—

$$h = \sqrt{\frac{K_W}{K_B C}\left(1 + \frac{K_B}{C}\right)} \quad . \quad . \quad . \quad (8)$$

And for a very high hydrolysis

$$h = \frac{\sqrt{\frac{1}{C} \cdot \frac{K_W}{K_B}}}{\sqrt{1 + \frac{K_W}{4CK_B}} + \sqrt{\frac{K_W}{4CK_B}}} \quad . \quad . \quad (9)$$

The ionisation co-efficients $a_A$, etc., in the equations (3*a*) to (4*b*), (7*a*) and (7*b*) can in most cases be only approximately estimated.

The degrees of hydrolysis corresponding to given dissociation constants and dilutions may most easily be obtained by interpolation from a curve, plotted by means of the tables given below.

The first has been calculated by Lunden,‡ the second by Bjerrum for a temperature 22°—24° C., at which $K_W = 1 \times 10^{-14}$.

| $K/K_W =$ | $10^6$ | $10^5$ | $10^4$ | $10^3$ | $10^2$ | 10 |
|---|---|---|---|---|---|---|
| $K =$ | $10^{-8}$ | $10^{-9}$ | $10^{-10}$ | $10^{-11}$ | $10^{-12}$ | $10^{-13}$ |

| *Dilution.* | *Degrees of Hydrolysis.* | | | | | |
|---|---|---|---|---|---|---|
| V = 10 | 0·0032 | 0·0100 | 0·0311 | 0·0955 | 0·270 | 0·618 |
| V = 100 | 0·0100 | 0·0311 | 0·0955 | 0·270 | 0·618 | 0·916 |
| V = 1000 | 0·0311 | 0·0955 | 0·270 | 0·618 | 0·916 | 0 990 |

| K = | $10^{-2}$ | $10^{-4}$ | $10^{-6}$ | $10^{-8}$ |
|---|---|---|---|---|
| *Dilution.* | *Degrees of Hydrolysis.* | | | |
| V = 1 | $10^{-6}$ | $10^{-5}$ | $10^{-4}$ | $10^{-3}$ |
| 10 | $3{\cdot}3\times10^{-6}$ * | $3{\cdot}2\times10^{-5}$ | $3{\cdot}2\times10^{-4}$ | $3{\cdot}2\times10^{-3}$ |
| 100 | $1{\cdot}4\times10^{-5}$ * | $10^{-4}$ | $10^{-3}$ | $10^{-2}$ |
| 1,000 | $1{\cdot}05\times10^{-4}$ * | $3{\cdot}3\times10^{-4}$ * | $3{\cdot}2\times10^{-3}$ | 0·032 † |

* Calculated by formula (8).
† Calculated by formula (9).
‡ Ahrens' Sammlung XIV.

The extension of these calculations to any desired temperatures or dilutions is obvious. The agreement with experimental results is not always good since a trace of excess acid or base has a particularly great influence upon the [H·] of such solutions (see Chap. V., p. 191).*

The following well-known experimental results of Walker, Shields, Bredig, and others may be used as examples of the general validity of the tables.

*Salts of Weak Acids* (concentration = 0·1 N).

| Salt | $CH_3COONa$ | NaHS | $NaBO_2$ |
|---|---|---|---|
| Per cent. Hydrolysis | 0·008 | 0·14 | 0·84 |

| Salt | NaCN | $C_6H_5ONa$ |
|---|---|---|
| Per cent. Hydrolysis | 0·96 | 3·0 |

*Salts of Weak Bases* (concentrations = N/32).

| Salt | $C_6H_5 \cdot NH_2 \cdot HCl$ | $C_6H_4(C^4H_3) \cdot N^1H_2 \cdot HCl$ |
|---|---|---|
| Per cent. Hydrolysis | 2·6 | 1·5 |
| Hydrochloride of | Aniline. | Paratoluidine. |

| Salt | $C_6H_4(C^2H_3) \cdot N^1H_2 \cdot HCl$ | $CO(NH_2)_2 \cdot HCl$ |
|---|---|---|
| Per cent. Hydrolysis | 3·1 | 95·0 |
| Hydrochloride of | Orthotoluidine. | Urea. |

If the dissociation constants are known independently they may be used to verify the values of $K_W$, as has been done in many cases. Conversely the results of hydrolysis measurements are widely used to determine $K_A$ or $K_B$. The actual [H·] and [OH'] of the solutions have been used to determine the degrees of hydrolysis, and may be obtained

* The hydrolysis corresponding to intermediate constants may be interpolated on a graph similar to that given.

from the latter by the inverse calculation in simple cases.

Thus, for 0·1 KCN $[OH'] = 0{\cdot}1 \times 0{\cdot}01$.

When the hydrolysis takes place in steps, as with salts of polyvalent metals, the degrees of hydrolysis cannot be calculated with any certainty from [H·] or [OH'].

This does not, of course, impair the utility of the experimental values of [H·] *e.g.*, as determined by the hydrogen electrode (Bjerrum, *Zeitsch. phys. Chem.*, 59, 336 (1907); Denham, *J. Chem. Soc.*, 93, 41 (1908) ).

The result for aniline hydrochloride may be compared with that given above.

*Aniline Hydrochloride.*

| Dilution V = | 16 | 24 | 32 |
|---|---|---|---|
| [H·] = | 0·00114 | 0·00097 | 0·00081 |

*Chromium Chloride* (*blue*).

| V = | 4 | 8 | 16 | 32 | 64 |
|---|---|---|---|---|---|
| $10^2[H\cdot]$ = | 0·417 | ·296 | ·234 | ·176 | ·135 |

*Aluminium Chloride.*

| V = | 16 | 32 | 64 | 100 | 128 |
|---|---|---|---|---|---|
| $10^2[H\cdot]$ = | $0{\cdot}152_0$ | $0{\cdot}114_0$ | $0{\cdot}080_7$ | $0{\cdot}062_6$ | $0{\cdot}057_7$ |

The [H·] derived from solutions of $Al_2(SO_4)_3$ is of the same order, being somewhat lower at higher salt concentrations and higher at lower concentrations.

In some cases no equilibrium potential of the hydrogen electrode was obtained, probably owing to the formation of colloidal complexes of basic salts.

At 100° the acidity derived from the hydrolysis of salts of aluminium, etc., is about twice as great as at 18° (Ley, *Zeitsch. phys. Chem.*, 30, 193 (1899) ).

*Some Methods of finding the Degree of Hydrolysis, and Hydrion or Hydroxylion Concentration.*

*Conductivity.*—The calculation of the degree of hydrolysis from conductivity measurements alone requires a knowledge of the mobilities of all ions as well as of the degrees of ionisation of the salts, etc.

The hydrolysis of a binary salt of, *e.g.*, a strong acid and weak base may be obtained from a knowledge of the molecular conductivity of the hydrolysed salt $\Lambda_X$ of the acid and at the concentration which would be produced by complete hydrolysis $\Lambda_A$ and of the unhydrolysed salt $\Lambda_S$. The last datum may be obtained either from the ionic conductivities and the degree of dissociation of a salt of the same type or from the conductivity of a solution in which the hydrolysis has been driven back, *e.g.*, by the addition of the strong acid, the conductivity of which is, of course, subtracted.

The degree of hydrolysis $x$ is then given by—

$$x = \frac{\Lambda_X - \Lambda_S}{\Lambda_A - \Lambda_S}$$

The method is not suitable for the very weakest acids and bases, nor for those which are so strong that $100x$ is less than 2 or 3. It is most applicable where $K_A$ or $K_B$ lie between $1 \times 10^{-9}$ and $1 \times 10^{-12}$ (Lunden, *loc. cit.*, p. 32).

*Catalysis by H· and OH'.*—The proportionality of the velocities of many reactions to the concentration of the hydrion or hydroxylion by which they are catalysed has been of the greatest service in confirming the results of conductivity measurements. Later work has shown that the catalytic method is subject to certain restrictions. Thus the presence of neutral salts has an accelerating influence which is not accounted for by known causes, such as the double decomposition which must occur to some extent between a weak acid and, *e.g.*, NaCl.

Thus the rate of inversion of cane-sugar by 0·05N· HCl after all corrections have been made is increased by 11·7 per cent. in a solution 0·125N· with respect to KCl (Arrhenius, *Zeitsch. phys. Chem.*, 31, 197 (1899)).

The velocity constant of a unimolecular reaction is given by the equation—

$$K = \frac{1}{t_2 - t_1} \log \frac{a - x_1}{a - x_2}$$

$a$ = initial concentration of changing molecules.
$x_1$ and $x_2$ = amounts changed in times $t_1$ and $t_2$.

If $K_1$ is determined for a hydrolysed chloride of a given concentration and $K_2$ for hydrochloric acid of the same concentration, then the degree of hydrolysis $= \frac{K_1}{K_2}$

The velocity constants have high temperature co-efficients which are not the same as the (low) temperature co-efficient of hydrion concentration. Careful work in thermostats is therefore necessary. The accuracy is about 1 or 2 per cent. in K.

Among the reactions used for this purpose are the inversion of cane sugar, the formation and decomposition of esters, the decomposition of diazo compounds.

Full details of the first two methods are given in most text-books of practical physical chemistry. Other reactions have been proposed from time to time which often have special advantages.

Thus the hydrolysis of ethyl diazoacetate to form ethyl glycollate and nitrogen, which is measured appears to be extraordinarily sensitive to very low values of [H·] (Curtius, Bredig and Fraenckel).

Calcagni, *Gazz. Chem. Ital.*, 44, ii., 447 (1914), has used this reaction to determine the [H·] of phenols.

$$N_2 : CH{\cdot}COOC_2H_5 + HOH = CH_2OH{\cdot}COOC_2H_5 + N_2.$$

The ratio of the velocity constant K to [H·] was found to be constantly 38·5 for all strong and weak acids. The strength of the phenols was found to increase with the number of hydroxyl groups.

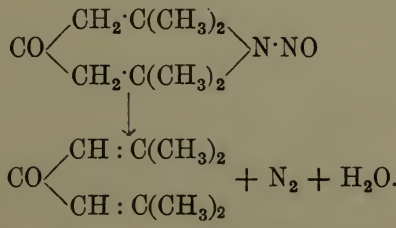
| Phenol $C_6H_5OH$ | catechol $C_6H_4(OH)_2$ | pyrogallol $C_6H_3(OH)_3$ |
|---|---|---|
| $10^5[H\cdot] = 0{\cdot}37$ | 0·96 | 3·4 |

Aliphatic alcohols did not produce any decomposition.

If catalytic methods are used to find the [H·] of moderately concentrated acids, a correction must be introduced for the accelerating effect of the undissociated acid. The correction is small in the case of weak acids, large in that of strong acids (see *Chem. Soc. Ann. Reports*, IX., 25 (1912)).

Since hydroxylion concentrations are in most cases deduced from hydrion concentrations through the water constant, an independent method of determining the former has a great value. A reaction which allows of the comparison of different [OH′] by means of their catalytic power has been described from the University of Bristol (Clibbens and Francis, *J. Chem. Soc.*, 101, 2358 (1912); Francis and Geake, *J. Chem. Soc.*, 103, 1722 (1913)).

Nitrosotriacetonamine is decomposed by alkalies into phorone and nitrogen.




The velocity of the reaction is measured by the volumes of nitrogen, $V_1$, $V_2$ and $V_\infty$, evolved at times $t_1$, $t_2$, minutes,

and when the reaction is complete, from about 0·13 grams of the compound.

$$\text{It was found that } -\frac{2{\cdot}303}{t}\log\frac{Va - V_1}{Va - V_2} = K.$$

This constant of a unimolecular reaction when divided by [OH′] (determined by the conductivity) was also constant at constant temperature and over a range of [OH′] from about 0·002 to 0·05.

Thus at $t = 30°$.

| | $Ba(OH)_2$ | KOH | $N(CH_3)_4OH$ |
|---|---|---|---|
| $K/[OH'] =$ | 1·96 | 1·93 | 1·91 |

| | $N(C_2H_5)_4OH$ | sodium phosphates. |
|---|---|---|
| $K/[OH'] =$ | 1·94 | 1·94 |

The fluctuations seem to be due rather to unavoidable errors in K than to any specific influence of the other ions present.

Between [OH′] = 0·05 and OH′] = 0·3 the method is inapplicable, but can again be used, though with a diminished accuracy, from 0·3 to 1·4.

From another series of experiments in the neighbourhood of 40° it was shown that the change of catalytic power with temperature is given by the equation—

$$[OH'] = \frac{K_t}{R} + R = 1{\cdot}96 \times 0{\cdot}22\,(t - 30).$$

The method should therefore have an application in determining the temperature co-efficients of alkalinity. The presence of neutral salts ($NaNO_3$ and $Na_2SO_4$) has little effect on K if their concentration is below normal, but in higher concentrations they may reduce K to one-quarter or one-sixth of its former value.

In another paper (Francis, Geake and Roche, *J. Chem. Soc.*, 107, 1651 (1915) T.) the constant was defined in terms

of the pressures $p_a$, $p$, etc., which the gas exerts when reduced to constant volume, with the following results—

| | | | | | |
|---|---|---|---|---|---|
| $t$ | = 18 | 30 | 40 | 50 | 60 |
| K/[OH′] | = 0·62 | 1·92 | 4·52 | 10·14 | 19·6. |

It was found also that the range of [OH′] from 0·05 to 0·5 can be determined with the aid of (*a*), nitrosovinyl diacetonamine, (*b*) nitrosoisobutyl diacetonamine.

| | | | | |
|---|---|---|---|---|
| (*a*) | $t$ | = | 40 | 50 |
| | K/[OH′] | = | 0·171 | 0·553 |
| (*b*) | $t$ | = | 40 | 50 |
| | K/[OH′] | = | 0·241 | 0·714 |

*Distribution Ratio.*—The concentration of undissociated molecules in the solution may be determined independently of that of the ions by taking advantage of the constancy of the ratio of their concentration in the dissociating solvent and in an organic solvent or in the vapour phase.

The method is useful for very weak as well as moderately weak acids and bases. It has also been used by Rothmund and Drucker to determine the ionisation constant of picric acid (see also B. de Szyszkowsky, p. 26).

Veley has determined the hydrolysis of aniline hydrochloride by shaking it with benzene, and that of ammonium salts by distillation of the free ammonia (*J. Chem. Soc.*, 79, 863 (1901); 87, 26 (1905); Veley and Warth, 85, 1713 (1904)).

*Change of Solubility.*—If a slightly soluble acid or base is treated with an alkaline or acid solution, the solubility is increased by an amount which is proportional to the salt formed. The concentration of the free acid (or base) is equal to the saturation concentration in pure water. Thus the dissociation constant of the solid electrolyte may be found by varying the amounts of strong base or acid. The

amount of a weak acid dissolved in water is $[HA]_S$ (saturated solution), whereas the total acid dissolved by a solution of NaOH is

$$[HA]_S + [A'] + [BaA].$$

Now if $[BA] = 0$, *i.e.*, all the salt is ionised,

then $[A']$ = solubility of acid in NaOH − solubility of acid in water

Also $[OH']$ = free NaOH $\times a_B$ and if $a_B$ is nearly 1 as in dilute solutions

then $[OH']$ = total NaOH − salt = $[NaOH] - [A']$

and $\dfrac{K_A}{K_W} = \dfrac{[A']}{[HA]_S \times [OH']}$* is entirely expressed in experimental magnitudes.

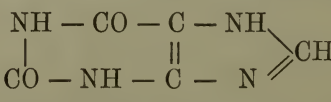
So, also, for a weak and slightly soluble base

$$\frac{K_B}{K_W} = \frac{[B\cdot]}{[BOH]_S \times [H\cdot]}$$

Thus either $K_B$ or $K_A$ may be determined by measuring the increase of solubility. The solubility of an amphoteric electrolyte is at a minimum at a given $[H\cdot]$ which is usually not far removed from the neutral point (isoelectric point). The solubility is increased by both acids and alkalies. Thus casein dissolves either in strong acids or alkalies, and is coagulated in slightly acid solutions ($-\log [H\cdot] = 4{\cdot}4$).

If alkalies raise the solubility more than acids, then $K_A > K_B$ and *vice versâ*. The constants of the amphoteric

xanthine



have been investigated in this way by Wood, *J. Chem. Soc.*, 83, 568 (1903); 89, 1831 (1906).

* See p. 11, equation (1*a*).

At a temperature of 40·1° this compound dissolves in water to the extent of 0·1823 grams to the litre.

In 0·1 N· HCl the solubility is 0·2183 grams, and in 0·05 N· NaOH 6·405 grams to the litre.

From these results (if $K_W = 3{\cdot}15 \times 10^{-14}$) $K_B$ is $6{\cdot}09 \times 10^{-14}$ and $K_A$ is $1{\cdot}186 \times 10^{-10}$.

The constancy of the solubility may also be used to prepare solutions of known [H·] (see p. 184), and conversely, a determination of [H·] and total amount dissolved $C_s$ may be used to calculate the solubility of the weak acid $[HA]_S$.

$$\text{For } C_s = \frac{[HA]_s}{1-a} = [HA]_s \cdot \frac{[H] + K}{[H\cdot]}.*$$

*The Hydrogen Electrode.*—This useful method of measuring [H·] depends upon the fact that a definite potential difference exists between a platinum or palladium electrode saturated with hydrogen gas at a given pressure, and a solution of definite acidity or alkalinity in which it is immersed. The original standard of hydrion concentration may be determined by the conductivity or in any other independent manner, and when this is done the difference of potential between the platinum hydrogen [Pt $H_2$]. electrode in this solution (1) and the same electrode in a solution of different acidity (2) may be used to calculate the [H·] value of (2) according to the method given below. This value agrees with the [H·] of (2) as independently determined by conductivity, etc.

*Apparatus.*—The electrode consists generally of platinum foil or wire platinised (covered with finely divided platinum) or of glass on the surface of which platinum has been burnt by a well-known receipt. Palladium or gold have also been used. The electrode is partly immersed in the solution and the upper part is surrounded by pure hydrogen. The two

* See p. 13.

half cells are connected together by siphons filled with the solutions and dipped into a connecting vessel which is filled

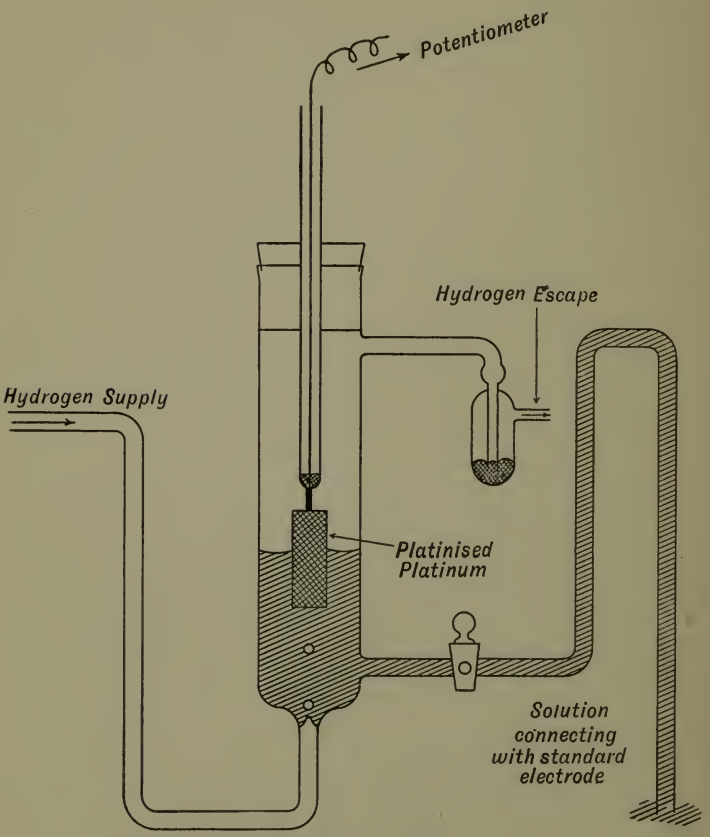



Fig. 1.

with one solution or with KCl solution, etc. (see p. 45). Metallic connection with the electrodes which are sealed into glass tubes is made by a drop of mercury.

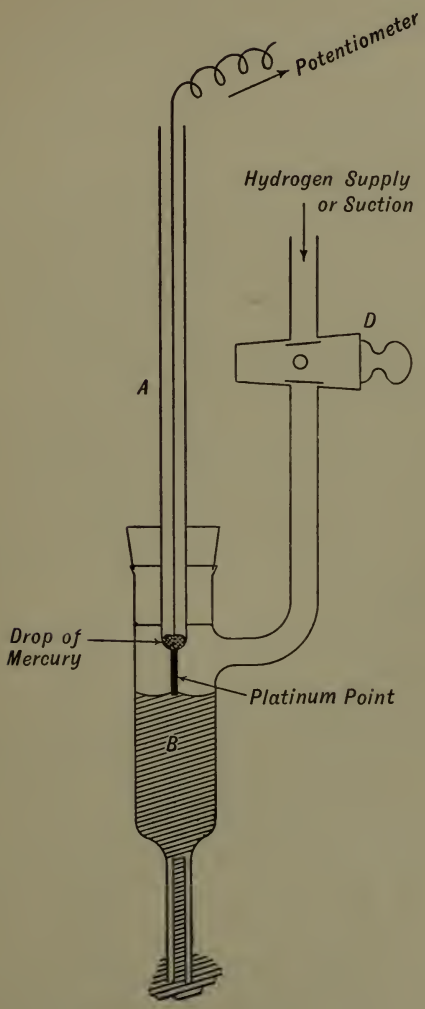

Potentiometer
Hydrogen Supply
or Suction
D
A
Drop of
Mercury
Platinum Point
B

FIG. 2.

The whole system is represented diagrammatically by

| $H_2Pt$ | Solution (1) | Connecting Solution | Solution (2) | $H_2Pt$ |
|---|---|---|---|---|

The form of electrode vessel varies according to the purpose for which it is required.

In the first class, Fig. 1, a continuous current of hydrogen is passed through the liquid and over the electrode, and passes out through a small wash-bottle containing mercury, which prevents any suck back of air when the current of hydrogen is discontinued. Suitable forms have been described by Wilsmore, *Zeitsch. phys. Chem.*, *loc. cit.*, p. 86, and Sorensen *Biochem. Zeitsch.*, *loc. cit.*, p. 91. In the second class, Fig. 2, hydrogen is passed into the filled cell, displacing some liquid, and the liquid is shaken until saturation of the liquid and electrode with hydrogen is complete and the E.M.F. reaches a steady value. Equilibrium is attained very rapidly if the electrode terminates in a point which only just touches the surface of the liquid. The object of this procedure is to avoid loss of $CO_2$ from liquids which owe their acidity to the balanced neutrality of carbonates, or to avoid other changes which would result from contact with a continuous current of hydrogen. In physiological work also it is important to avoid frothing, and only small quantities of liquids may be available.

G. S. Walpole has described a simple form of electrode vessel and filler* with which measurements can be made very rapidly (*Biochem. J.*, 7 (4) 413 (1913)). The hydrogen electrode vessel is connected with another half-cell, which may consist of another hydrogen electrode or of some other standard cell, and the E.M.F. of the whole combination $E_1 - E_2$ is measured by the compensation method in which

* A glass syringe connected by a side tap with the hydrogen supply.

$E_1 - E_2$ is balanced against a steady fall of potential, *e.g.*, from an accumulator cell, and which has been calibrated by means, *e.g.*, of a standard cadmium cell.

The balance of potential is shown by absence of movement in a galvanometer or capillary electrometer in the circuit. For the details any text-book of practical physical chemistry may be consulted (see also Chap. VI., p. 270).

*Diffusion Potential.*—In addition to the differences of potential at the two electrodes, there are in general others at the surfaces of contact between solutions of the same substances at different concentrations or of different substances at the same or different concentrations. They amount in general only to a few millivolts, except in the case of the strongest acids or alkalies. They may sometimes be calculated and subtracted from the total E.M.F., sometimes measured by special devices, but in general are eliminated or reduced to less than a millivolt.

One method of accomplishing this is to make up all solutions of the same concentration with respect to some neutral salt, *e.g.*, NaCl. Thus Salm and others have used physiological salt solution (0·125 N. NaCl).

A better method, however, is to use as connecting fluid a salt such as KCl in high concentration (Nernst-Bugarsky, *Zeitsch. anorg. Chem.*, 14, 150 (1897)), or $NH_4NO_3$ (Cumming, *Trans. Far. Soc.*, 2, 213 (1907)).

These two electrolytes fulfil the conditions which are required for an eliminator of diffusion potential.

(1) Solutions of high concentration may be prepared.

(2) The velocities of the two ions are approximately equal.

Ammonium nitrate cannot be used in contact with an alkaline solution, since ammonia is set free.

Potassium chloride can be used in most cases. Where there is reason to believe that the diffusion potential is

small, a saturated or nearly saturated solution may be considered effective, without any further calculation. In other cases it may be necessary to use the device of Bjerrum, *Zeitsch. phys. Chem.*, 53, 428 (1905), *i.e.*, to take measurements with 1·75 N and 3·5 N · KCl, and to extrapolate the E.M.F. curve so obtained. The difference between the potentials with these two concentrations of connecting solution is only about 2—4 millivolts, except in the case of strongly acid solutions.

*The Calculation of Hydrion Concentration from Electromotive Force.*

The relation between the E.M.F. of the combination figured on p. 44 and the hydrion concentrations $[H^{\cdot}]_1$ and $[H^{\cdot}]_2$ may be deduced from thermodynamical principles by considering the work required to transfer 1 gram ion of hydrogen osmotically in any reversible manner from solution (1) to solution (2).

$$E = \frac{RT}{F} \log (\text{nat.}) \frac{[H^{\cdot}]_1}{[H^{\cdot}]_2},$$

F being the electrochemical unit quantity of electricity, = 96,540 coulombs, R the gas constant (in joules) and T the absolute temperature.

Substituting the numerical values

$$E = 0{\cdot}0_3198T \log \frac{[H]_1}{[H]_2} \text{ volts},$$

and at 18°

$$E = 0{\cdot}0577 \log \frac{[H^{\cdot}]_1}{[H^{\cdot}]_2}.$$

For example, if solution (1) contains 0·01 N · HCl and (2) 0·001 N · HCl, then

$$\log \frac{[H^{\cdot}]_1}{[H^{\cdot}]_2} = 1 \text{ nearly},$$

and E is found to be almost exactly 58 millivolts.

The standards of acidity may be chosen from those on p. 187.

Thus Salm used 0·0104 HCl 0·1 N with respect to NaCl, a solution which according to his calculation is 0·01 N with respect to $H^{\cdot}$.

Other solutions were measured against this, and their $[H^{\cdot}]$ values calculated as above.

It is perhaps more convenient to determine once and for all the total difference of potential between the standard to be used and a hydrogen electrode in normal hydrion.

This fixed potential ${}_{0}E_{s}$ is then subtracted from the potential ${}_{s}E_{x}$ of the unknown against the standard electrode (${}_{s}E_{x}$). The potential ${}_{0}E_{x}$ thus obtained will be that of the electrode in question against 1 N · $H^{\cdot}$, and the calculation is simplified to—

$$E \text{ (corrected)} = 0{\cdot}0_3\,198T \log \frac{1}{[H^{\cdot}]}.$$

Some values of $0{\cdot}0_3198T$ are given on p. 54.

Thus suppose that a hydrogen electrode in $[H^{\cdot}]_x$ gave 0·5 volts against a normal hydrogen electrode at 19°.

$$-\log [H^{\cdot}]_x = \frac{0{\cdot}5}{0{\cdot}058} = 8{\cdot}62$$

and

$$[H^{\cdot}]_x = 2{\cdot}4 \times 10^{-9}.$$

The single potential of a normal hydrogen electrode is defined as that of the $H_2Pt$ electrode in a solution normal with respect to $[H^{\cdot}]$ (*i.e.*, 1·25 N · HCl).

It has been made the zero or reference point of potentials generally, and its value was determined by Wilsmore (*Zeitsch. phys. Chem.*, 35, 296 (1900)). A re-determination of this important constant has also been made by Sorensen (see p. 50).

*Standard Half-cells for Measuring [H·] by the Hydrogen Electrode.*

The actual use of a solution of normal hydrion in a combination is undesirable for several reasons.

One of the following may be chosen according to circumstances.

*Millinormal HCl and Tenth Normal KCl.*

The diffusion potential of this against concentrated HCl is very small. The degree of dissociation is 0·84 and [H·] is therefore $0{\cdot}0_384$.

The correction of potentials measured against this to normal [H·] follows from the statements of p. 46.

Let ${}_0E_x$ be the required E.M.F. of normal hydrion against an unknown $[H\cdot]_x$.

${}_0E_S$ be the E.M.F. of [H·] = 1 against the above standard [H·] (or against any of the standards given below).

${}_sE_x$ be the measured E.M.F. of $[H\cdot]_S$ against $[H\,]_x$.

$$\text{Then } {}_0E_x = {}_0E_S + {}_sE_x \quad . \quad . \quad . \quad . \quad (1)$$

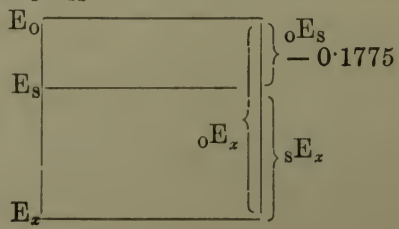
$$\text{and } {}_0E_S = 0{\cdot}0_31983T \log \frac{1}{0{\cdot}0_384} = -0{\cdot}1775$$

at $t = 18°C$.

$$\text{Hence } {}_0E_x = -0{\cdot}1775 + {}_sE_x$$

$$\text{or } -\log [H\cdot]_x = \frac{{}_0E_x - 0{\cdot}1775}{0\ 0_31983T}.$$

The potentials are shown by the sketch which represents $[H\cdot]_x$ as less than $[H\cdot]_S$.



ERRATA.

Page 48. For $-0{\cdot}1775$ read $+0{\cdot}1775$.

Page 48 (third line from bottom of page). For ${}_{0}E_{x}$ substitute ${}_{s}E_{x}$

*Standard Acetate Mixture.*

This mixture also recommended by Michaelis possesses the advantage of a more exactly defined [H·] and a greater freedom from diffusion potential. It consists of 50 c.c. of N · NaOH with 100 c.c. of N · $CH_3COOH$ + 350 c.c. of water. It is 0·1N. with respect to free acetic acid and sodium acetate, and has a hydrion concentration calculated and found of $2{\cdot}35 \times 10^{-5}$. The [H·] of this solution is only slightly dependent on temperature.

| $t =$ | 15 | 18 | 21 | 25 | 38 |
|---|---|---|---|---|---|
| $10^5$ [H·] = | $2{\cdot}3_0$ | $2{\cdot}3_5$ | $2{\cdot}3_6$ | $2{\cdot}3_4$ | $2{\cdot}3_0$ |
| $-\log$ [H·] = | $4{\cdot}63_8$ | $4{\cdot}62_3$ | $4{\cdot}62_7$ | $4{\cdot}63_1$ | $4{\cdot}63_8$ |

The potentials of this solution against the calomel electrode are given on p. 54.

*Other Standard Electrodes.*

The standard hydrogen electrodes may for many purposes be replaced by others, of which the most frequently used are those made up of Hg, HgCl and KCl. The potential difference between a hydrogen electrode and these may be considered as made up of two single potentials, one between the $H_2Pt$ and its solution, the other between the Hg and its solution.

The absolute potentials of the calomel electrodes are :—

Normal KCl calomel

$$E = + 0{\cdot}5600 + 0{\cdot}0006\ (t - 18) \pm 0{\cdot}0_45.$$

Decinormal KCl calomel

$$E = 0{\cdot}612 + 0{\cdot}0008\ (t - 18).$$

When unknown acid solutions are measured against KCl calomel electrodes, the [H·] may be obtained by the calculation already given, the potential difference ${}_0E_S$ in

equation (1), p. 48, being that of the calomel against normal hydrion electrode. The potential of the decinormal calomel against normal hydrion electrode has been carefully determined by Sorensen, *Biochem. Zeitsch.*, 21, 131 (1909), and from it the single potential of the normal hydrion electrode calculated.

The acid concentration in the hydrogen electrode vessel was varied, but NaCl was always added in such amount that the solution was decinormal with respect to total chloride. According to the principle of Arrhenius the degree of dissociation is then constant, and it was taken as 0·9165. As the result of many measurements

$$_0E_S = E - 0{\cdot}0577 \log \frac{1}{[H\cdot]}$$

$$= 0{\cdot}3377 \text{ at } 18°.$$

Hence the single potential $_0e_H$ of the normal hydrogen electrode

$$= + 0{\cdot}613 - 0{\cdot}338 = + 0{\cdot}275 \text{ at } 18°.$$

Wilsmore's value, *loc. cit.*, p. 47, is + 0·277 at 25°.

According to Auerbach, *Zeitsch. Electrochem.*, 1912, the E.M.F. of the normal hydrogen electrode against decinormal KCl calomel is constantly

$$+ 0{\cdot}337 \text{ from } 0° \text{ to } 30°.$$

The temperature coefficient was also shown to be zero by means of the equation

$$E = \frac{Q}{nF} + T\frac{dE}{dT},$$

in which Q is the calorimetric heat of the reaction which occurs when current is taken from the cell.

*Correction of Hydrogen Potential for Temperature and Pressure.*

One disadvantage inherent in the use of an electrode of a different nature as a standard in hydrion measurements is that it is necessary to reduce the single potentials of the $H_2Pt$ half-cell to standard conditions. Any change of temperature will affect the single potentials of the calomel and hydrogen unequally, while a change in the partial pressure of the hydrogen will of course affect the latter half alone.

*Temperature.*—The total temperature coefficient of the hydrogen electrode is small. It is probably made up of factors some of which are inaccessible to the present kinds of experiment. Among those which may be estimated are the change in the factor $0{\cdot}0_31981$ T used in calculating-log [H·], and the change in pressure of water vapour and of any gases which are dissolved in the solution to be measured.

*Pressure.*—A change in the pressure of hydrogen in contact with the electrode will alter the thermodynamical potential of the hydrogen in the platinum, and therefore also the single potential of the hydrogen electrode. A correction $E_1 - E_p$ will have to be added in order to reduce the readings to normal pressure. If the pressure is decreased the + potential of the hydrogen is increased, and therefore the difference between this and the calomel decreased.

The correction is

$$E_1 - E_p = -\frac{RT}{2F} \log \frac{p}{1}.$$

Thus if the pressure were 740 mm. at 18° C.,

$$E_1 - E_p = \Delta E = -\frac{0577}{2} \log \frac{740}{760}$$
$$= 0{\cdot}0_333 \text{ volt.}$$

The correction for the usual barometric fluctuations need not therefore be made except in the case of highly accurate measurements.

The partial pressure $p$ of the hydrogen is, of course, obtained in the usual way by the subtraction of the partial pressures of other gases, including water vapour from the total pressure.

For example, if the liquid contains a large amount of free carbonic acid, say 25 per cent., the correction becomes

$$\Delta E = -\frac{0{\cdot}0_31983}{2}(273+18)\log\frac{3}{4}$$
$$= 0{\cdot}0036 \text{ volt.}$$

The following are the corrections for change of pressure which are to be added to the observed value of a hydrogen against any calomel electrode at room temperature :—

| $pH_2$ (atmospheres) . | . 1 | 0·95 | 0·9 | 0·8 | 0·7 | 0·6 | 0·5 |
|---|---|---|---|---|---|---|---|
| $\Delta E$ (millivolts) . | . 0 | 0·6 | 1·3 | 2·9 | 4·5 | 6·4 | 8·7 |

The correction for the pressure of water vapour becomes more important at higher temperatures.

Thus at 30° with a normal barometer

$$\Delta E = -\frac{0{\cdot}0601}{2}\log\frac{728}{760} = 0{\cdot}0_356 \text{ volt.}$$

The experimental E.M.F.'s for moist hydrogen may thus be reduced to dry hydrogen at standard pressure as in table, p. 54.

*The Determination of [H·] by Measurements with a Decinormal KCl Calomel Electrode.*

It is supposed that the difference of potential between a hydrogen electrode in the solution of unknown [H·] and the calomel electrode is ${}_sE_x$ at $t°$.

The potential is first reduced to normal pressure by the corrections just given.

Then

$$_0E_x = {}_0E_s + {}_sE_x,$$

in which $_0E_s$ has the values given in the table on p. 54 for dry or moist hydrogen at normal pressure

$$-\log [H\cdot]_x = \frac{{}_sE_x - {}_0E_s}{0{\cdot}0_31983T}.$$

Thus a neutral phosphate solution measured against a decinormal calomel at 18° gave an E.M.F. of 0·751 ± 0·002 volt.

$$\therefore -\log [H\cdot] = \frac{0{\cdot}751 - 0{\cdot}338}{0{\cdot}0577} = 7{\cdot}18.$$

*The Saturated KCl Calomel Electrode.*

The construction of this standard, as described by Michaelis, "Die Wasserstoffionen-Konzentration," differs from that of the normal and decinormal cells only in the particular that the solution is saturated with KCl as well as with HgCl, and crystals of KCl are always present. The taps and other junctions on which a crust of KCl is apt to form are well greased with vaseline. The potentials are as constant as those of other standard calomel electrodes. It will be noticed from the table on p. 54 that the temperature coefficient of the normal hydrogen-calomel combination is much less in the case of the decinormal than in that of the saturated KCl calomel electrode. But in the latter case the temperature coefficient of E.M.F. is almost equal to that of the factor 0·000198T, and, therefore, any particular number of millivolts corresponds nearly to the same values of [H·] at all ordinary temperatures.

| Temperature | 0·1 KCl HgCl Normal [H·] Dry $H_2$. | 0·1KCl HgCl Normal [H·] Moist $H_2$. | Saturated KCl HgCl. | $2{\cdot}303\frac{RT}{F}$ |
|---|---|---|---|---|
| 0° | 0·337 | — | — | $0{\cdot}0541_5$ |
| 15 | — | — | 0·2525 | 0571 |
| 16 | — | — | 0·2517 | 0573 |
| 17 | — | — | 0·2509 | 0575 |
| 18 | 0·3377 | 0·3380 | 0·2503 | 0577 |
| 19 | — | — | 0·2495 | 0579 |
| 20 | 0·3375 | 0·3378 | 0·2488 | 0581 |
| 21 | — | — | 0·2482 | 0583 |
| 22 | — | — | 0·2475 | 0585 |
| 23 | — | — | 0·2468 | 0586 |
| 24 | — | — | 0·2463 | 0589 |
| 25 | — | — | 0·2458 | 0591 |
| 30 | 0·3364 | 0·3370 | — | 0601 |
| 37 | — | — | 0·2355 | 0615 |
| 38 | — | — | 0·2350 | 0617 |
| 40 | 0·3349 | 0·3359 | — | 0621 |
| 50 | 0·3326 | 0·3344 | — | 0641 |
| 60 | 0·3290 | 0·3321 | — | $0660_5$ |

| Temperature. | 0·1 KCl HgCl $H_2$Pt Standard Acetate. | Saturated KCl HgCl $H_2$Pt Standard Acetate. |
|---|---|---|
| 15° | 0·6025 | 0·5170 |
| 16 | — | 0·5171 |
| 17 | — | 0·5172 |
| 18 | 0·6045 | 0·5174 |
| 19 | — | 0·5175 |
| 20 | — | 0·5178 |
| 21 | 0·6075 | 0·5180 |
| 22 | — | 0·5183 |
| 23 | — | 0·5186 |
| 24 | — | 0·5190 |
| 25 | — | 0·5195 |
| 35 | — | 0·5200 |
| 38 | — | 0·5205 |

The results of measurements with the hydrogen electrode have on the whole confirmed and added confidence to the [H·] values obtained by conductivity, etc. Thus Walpole, *J. Chem. Soc.*, 105, 2525 (1914), has obtained the E.M.F. corrected for diffusion potential of a hydrogen electrode in acetic acid solutions against the decinormal KCl calomel electrode. The dissociation constant may be calculated from the equation

$$K = \frac{[H\cdot]^2}{c - [H\cdot]}.$$

A small error in E.M.F. makes a large error in K. Nevertheless the values of K only vary between 1·7 and $2{\cdot}08 \times 10^{-5}$ with evidence of a slight maximum.

Those found by the conductivity method vary between 1·80 and $1{\cdot}85 \times 10^{-5}$ (H. C. Jones, Reports of the Carnegie Institution of Washington, No. 170).

The hydrogen electrode may also be used to measure the [H·] of neutral solutions (see the example on p. 53) and even of alkaline solutions.

If it is admitted that by the laws of chemical equilibrium such a low value of [H·] may be perfectly definite, it may still seem remarkable that it should be found experimentally. The errors in an ordinary chemical analysis have a definite minimum value, which at such a low concentration may become many times the whole value to be determined.

But from the equation on p. 46, it is evident that a constant error in E (say, $\pm$ 1 millivolt) corresponds to the same proportional error in [H·], whether these are high or low, provided only that they are well defined, as they are in solutions of balanced neutrality. Thus $[H\cdot] = 3 \times 10^{-7}$ in a phosphate mixture (see p. 204) is better defined than $[H\cdot] = 5 \times 10^{-4}$ in a pure aqueous solution of HCl.

*The Change of Hydrion and Hydroxylion with Temperature.*

The determination of the effect of changing temperature upon the [H·] and [OH′] of all solutions would appear in theory to require merely the application of the experimental methods already described. It has been seen, however, that the hydrogen electrode results are subject to a somewhat elaborate correction on account of the alteration in temperature and concentration of the gas. The conductivity method also requires the setting up of new standards, *i.e.*, the mobilities at limiting dilution of all the ions in question. The velocity constant would appear to be particularly suitable for this problem, since the constant varies rapidly with the temperature and gains in accuracy as this increases.

The conductivities of hydrolysed salts as well as those of the free acids and bases have been determined by Noyes and his co-workers in a platinum-lined bomb of special construction which could be closed steam-tight and heated by the vapours of boiling liquids.

The degrees of dissociation could be obtained from the limiting conductivities in the manner already described, p. 9, and hence also the dissociation constants.

*Ammonia.*

| | | | | | |
|---|---|---|---|---|---|
| $t =$ | 18 | 100 | 156 | 218 | 306 |
| * $10^6 \times K =$ | 17·2 | 13·5 | 6·28 | 1·80 | 0·093 |
| $t =$ | 0 | 25 | 50 | 75 | 125 |
| † $10^6 \times K =$ | 13·9 | 18·0 | 18·1 | 16·4 | 10·4 |

*Acetic Acid.*

| | | | | | |
|---|---|---|---|---|---|
| $t =$ | 18 | 100 | 156 | 218 | 306 |
| * $10^6 \times K =$ | 18·3 | 11·14 | 5·36 | 1·72 | 0·139 |

* Noyes, Kato and Sosman, *Zeitsch. phys. Chem.*, 73, 20 (1910).
† Kanolt, *J. Amer. Chem. Soc.*, 29, 1414 (1907).

The following results for smaller range of temperature are quoted in the monographs of Lunden and Michaelis (see Preface).

*Acetic Acid.*

| $t =$ | 8 | 10 | 15 | 18 | 20 | 25 | 38 |
|---|---|---|---|---|---|---|---|
| $10^5K =$ | $1{\cdot}81_9$ | $1{\cdot}81_9$ | $1{\cdot}84_3$ | $(1{\cdot}85_1)$ | $(1{\cdot}86_0)$ | $1{\cdot}84_9$ | $(1{\cdot}81_4)$ |
| $t =$ | 40 | 50 | | | | | |
| $10^5K =$ | $1{\cdot}79_7$ | $1{\cdot}72_8$. | | | | | |

The values in brackets are interpolated

| $t =$ | 10 | 15 | 25 | 40 | 50 |
|---|---|---|---|---|---|
| $10^5K =$ | $1{\cdot}82_8$ | $1{\cdot}85_3$ | $1{\cdot}85_6$ | $1{\cdot}80_4$ | $1{\cdot}73_5$. |

The maximum calculated from this series is at 22°. At this temperature the heat of ionisation of acetic acid must therefore be zero.

*Salicylic Acid.*

| $t =$ | 0 | 20 | 30 | 35 | 40 | 45 |
|---|---|---|---|---|---|---|
| $10^3K =$ | 0·85 | 1·04 | 1·09 | 1·06 | 1·12 | 1·13 |
| $t =$ | 50 | 60 | 70 | 80 | 90 | |
| $10^3K =$ | 1·14 | 1·11 | 1·07 | 1·01 | 0·95 | |

(Euler, *Zeitsch. phys. Chem.*, 21, 257 (1896); Schall, *Zeitsch. phys. Chem.*, 14, 701 (1894).)

*Boric Acid.*

| $t =$ | 15 | 25 | 40 |
|---|---|---|---|
| $10^{10}K =$ | 5·48 | 6·62 | 8·49 |

*Hydrocyanic Acid.*

| $t =$ | 18 | 25 | 40 |
|---|---|---|---|
| $10^{10}K =$ | 4·7 | 7·2 | 15·7 |

*Ammonia.*

| $t =$ | 0 | 10 | 15 | 18 | 25 | 40 | 50 |
|---|---|---|---|---|---|---|---|
| $10^5K =$ | 1·4 | 1·63 | 1·71 | 1·77 | 1·87 | 1·98 | 1·96 |

The maximum occurs at 45°.

*Urea.*

| $t =$ | 0 | 25 | 40 |
|---|---|---|---|
| $10^{14}K =$ | 0·67 | 1·5 | 3·8 |

*Aniline.*

| $t =$ | 18 | 25 | 40 |
|---|---|---|---|
| $10^{10}K =$ | 3·5 | 4·6 | 7·6 |

*Pyridine.*

| $t =$ | 18 | 25 | 40 |
|---|---|---|---|
| $10^{9}K =$ | 1·63 | 2·28 | 4·25 |

The detailed measurements on which these results are founded show that the rapid increase of conductivity with temperature is due chiefly to the increased mobility of the ions. The changes in the dissociation constants are much slighter—they may be positive or negative, and the constant often reaches a maximum below 100°. Thus the [H·] and [OH′] of weak acids and bases respectively may often actually decrease with rise of temperature as they do in the case of strong acids and bases (see tables, p. 26, this chapter).

On the other hand, on account of the rise in the water constant (see p. 7) the [OH′] of acids and the [H·] of bases must increase with the rise of temperature. For $K_w$ increases very rapidly, whereas the [H·] of acids and [OH′] of bases sometimes increases and sometimes decreases, and either change is relatively slight.

Thus for 0·01 N · HCl (Michaelis)

| $t =$ | 18 | 38° |
|---|---|---|
| $[OH'] =$ | $7·6 \times 10^{-13}$ | $3·6 \times 10^{-12}$ |
| $-\log [OH'] =$ | 12·12 | 11·44 |

And for 0·1 N. $NH_3$

| $t =$ | 18 | 38 |
|---|---|---|
| $[H·] =$ | $5·4 \times 10^{-12}$ | $2·5 \times 10^{-11}$ |
| $-\log [H·] =$ | 11·27 | 10·60 |

In contrast with the relatively small change in dissociation of acids or bases, is the relatively great change in hydrolysis.

This is well illustrated by ammonium acetate.

| $t =$ | 18 | 100 | 156 | 218 | 306 |
|---|---|---|---|---|---|
| % hydrolysis = | 0·35 | 4·8 | 18·6 | 52·7 | 91·5 |

In this case since the acid and base have constants of about the same magnitude, the increased hydrolysis is not accompanied by any marked change in [H·] or [OH′].

When an acid or alkaline hydrolysis is in question, however, the [H·] or [OH′] must be increased, in accordance with equation, p. 31, proportionally to $\sqrt{K_W}$, *i.e.*, to the increase in the ionisation of water.

The highest ratio of increase between 25° and 100° is, according to the lists of pp. 6, 7, about 7 or 9 to 1. If at the same time $K_A$ or $K_B$ diminish, this ratio may be somewhat exceeded.

The rate of increase of $K_W$ with $t$ rapidly falls off with rise of temperature, and $K_W$ appears to reach a maximum between 250° and 275°. The values of [H·] and [OH′] at the maximum are equal to more than $20 \times 10^{-7}$. This gives the limit of the amount of hydrolysis to be expected at higher temperatures in autoclaves, etc. It can be shown by thermodynamical theory that the heats of neutralisation, etc., must be profoundly modified at these temperatures.

The differential of $K_W$ with respect to $t$ has a very high value at ordinary temperatures, still a considerable value at 100°, but at higher temperatures it rapidly falls off. It is connected by a well-known equation with the heat Q of the reaction

$$H\cdot + OH' = H_2O + Q.$$

This is exceptionally large at ordinary temperatures, but must become much smaller at temperatures above 100°.

The heat of combination calculated from $K_W$ and $t$ agrees fairly well with that found from the heat of neutralisation of strong acids and bases.

$$Na^{\cdot} + OH' + H^{\cdot} + Cl' = Na^{\cdot} + Cl' + H_2O.$$

The thermochemical Q may be used to check the change of $K_W$ with $t$, and the mathematical relation referred to above serves to smooth the experimental values of $K_W$ (see tables, pp. 5 to 7). A collection of the values of Q has been made by Lorenz and Bohi, *loc. cit.*, p. 6.

Their own smoothed experimental values from the E.M.F. of a hydrogen electrode in acid against one in alkali (see p. 5) agree with those of Noyes from conductivity to 1 or 2 per cent.

Q is expressed in gram calories :—

$Q = 28{,}460 - 49{\cdot}5T\ (0 - 100)$ (Noyes).
$Q = 14{,}617 - 48{\cdot}5t$ (Wormann-Heydweiller).
$Q = 15{,}426 - 88{\cdot}9t$ (Lunden).

# CHAPTER II

## LIGHT ABSORPTION IN THE VISIBLE SPECTRUM AND COLORIMETRY

The visible spectrum. Tables of lines and approximate colours. The determination of absorption spectra. Colorimetry. Spectrophotometric measurements and the extinction coefficient. The laws of light absorption and the formation of coloured ions or molecules. Complex formation and colour.

In the preceding chapter a brief account has been given of the results arrived at by the investigation of solution equilibria by purely electro-chemical methods. Where indicators also take part in the change, optical methods are also available. These fall into three main classes :—

(1) The qualitative mapping of the absorption spectra.

(2) The quantitative determination of the intensity of colour in those cases in which only the intensity but not the character of the absorption bands alters. The methods are those of colorimetry, of which typical examples will be found in Chap. IV.

(3) The quantitative determination of the intensity of the absorption for each wave-length by spectrophotometric methods. If the specific extinction is determined for each wave-length, a most complete and fundamental knowledge can be obtained of the optical behaviour under various conditions.

(1) All dye-stuffs which possess any practical utility as indicators show a definite change in the position or intensity of the absorption bands for a given alteration in the acidity of the solution. Bands in the ultraviolet may be replaced by others in the visible spectrum (phenolphthalein), or bands may be transferred from one to another part of the visible spectrum (methyl violet). A change in the general character of the absorption spectrum is usually accompanied

by a marked change of colour as seen by the unaided eye. An investigation into the constitution of indicators demands a knowledge of absorption spectra; the tables of spectra are also useful for standardizing and controlling the purity of commercial indicators of indefinite composition, such as litmus, rosaniline, bases, etc.

The visible spectrum extends from about $\lambda = 760\ \mu\mu$ to $\lambda = 400\ \mu\mu$ ($1\ \mu\mu = 1$ millionth of a millimetre). The wave-lengths of reference as tabulated below are: (1) the Fraunhofer lines; (2) prominent lines in the emission spectra (vacuum tube) of gases and of mercury vapour; (3) lines in the characteristic flame spectra of some metals.

*Dark Lines in the Solar Spectrum B, C, D, etc.*

| Element. | Wave Length $\lambda\ \mu\mu$. | Approximate Limits of Colour. |
|---|---|---|
| (Air A . . . | 760) | |
| (Air B . . . | 687) | |
| Hydrogen C . . | 656 | |
| | | 647 red and orange |
| Sodium D . . | 589 | 586 orange and yellow |
| | | 535 yellow and green |
| Iron E . . . | 527 | |
| Magnesium *b* . . | 518 | |
| | | 492 green and blue |
| Hydrogen F . . | 486 | |
| | | 455 blue and indigo |
| Iron G . . . | 431 | |
| | | 424 indigo and violet |
| Hydrogen *h* . . | 410 | |
| Calcium H . . | 397 | |

*Spectrum of Hydrogen.**

| | | | | | |
|---|---|---|---|---|---|
| $\lambda = 767$ | 671 | 589 | 535 | 486 | 461 |
| red | red | yellow | green | blue | violet. |

*Spectrum of Helium.*

| | | | | | | |
|---|---|---|---|---|---|---|
| $\lambda = 706{\cdot}5$ | 668 | 587·5 | 501·5 | 492 | 471 | 447 |
| | red | | green | blue | blue | violet. |

*Spectrum of Mercury.*

| | | | | | |
|---|---|---|---|---|---|
| $\lambda = 623$ | 615 | 597 | 577 | 546 | 496 |
| red | orange | yellow | | green | green-blue. |
| $\lambda = 491{\cdot}5$ | 436 | 408 | 405 | | |
| | violet | violet | violet. | | |

*Spectra of Other Metals* (in flame).

| *Element.* | λ. |
|---|---|
| Potassium $\alpha$ | 770 |
| Lithium $\alpha$ | 671 |
| Lithium $\beta$ | 610 |
| Sodium | 589·5 |
| Thallium | 535 |
| Strontium | 461 |
| Potassium $\beta$ | 404·5 |

The apparent separation of these lines on a spectrophotograph will of course depend on the dispersion constants of the prism employed. In order to locate absorption bands it is necessary to know the readings of the micrometer scale corresponding to a sufficient number of wave-lengths. A calibration curve is constructed from these readings which are plotted against the wave-lengths λ, or frequencies $\frac{1}{\lambda}$.

* In these series greenish-yellow may be referred to as "green," orange-yellow as yellow, etc., for convenience.

A typical calibration is as follows (de Boisbaudran):—

| Element . | K | Li | Na | Tl | H$\beta$ | Sr | Ca |
|---|---|---|---|---|---|---|---|
| $\lambda$ . . | 768 | 670·6 | 589·2 | 534·9 | 486·1 | 460·7 | 396·8 |
| Scale division. | 65·5 | 80·78 | 100 | 118·4 | 141·75 | 157·6 | 216·33 |

The curve should be checked from time to time by the sodium line. The light which is to be absorbed may be any white light of sufficient intensity; sunlight, arc, Nernst glower, incandescent gas mantle, or osram.

The spectrometer is adjusted for minimum deviation, etc., in the usual way (see text-books of practical physics or physical chemistry). A direct vision spectroscope with scale in the side-tube is sufficient for many purposes.

The red and yellow field of the spectrometer should be as broad as possible in relation to the green and blue. A high dispersion is unnecessary, as the bands then appear too broad, and it is difficult to place the cross-wires accurately on the centre. The error in placing the maximum is about 0·01°, if the scale can be read with this accuracy, and about 0·05° for the broader bands. The weaker absorption bands can be observed by diminishing the light. At the red and violet ends it is often necessary to widen the slit, and therefore this should be symmetrical.

The solution and the spectrometer are best placed in a box blackened inside, with holes for the beam of light and for observation. The solution is placed in the beam of light and in front of the spectrometer slit. It may either be contained in a test-tube one to two centimetres in diameter, or in a hollow glass prism. In the latter case the light which illuminates the bottom of the slit may be made to traverse a greater thickness than that which illuminates the top. The effect of varying the thickness can therefore be seen at a glance.

It is often desirable to investigate the absorption brought about by different thicknesses and concentrations of the coloured compound. Change of concentration often causes new bands to appear or the ones first observed to disappear. This behaviour may be recorded by a series of photographs. If the photographic method is used the source of light should contain many lines of reference for which the wave-lengths are known. Suitable sources are arcs between electrodes of iron or of alloys containing Cd, Bi, Ag, etc. For the green and red parts orthochromatic plates are required. If the wedge device is used, a single photograph will show the intensities of the absorption bands and supply a ready means of recognising dye-stuffs. A good collection of those used as light-filters has been published by Wratten and Wainwright (Wratten Light Filters, Croydon, 1913).* The plates show the position and intensity of the bands with great clearness. The photographs were taken through a wedge of black glass, the thickest part of which only transmitted $\frac{1}{10000}$ of the incident light.

The difference in absorption brought about by change of solvent alone is usually not such as to confuse the character of one indicator with another, but it partly accounts for the variability in the results of different observers. Other reasons for this are probably slight differences in the preparations themselves, and the effect of change of concentration referred to above.

The spectrophotometric absorptions of some indicators as found by a uniform method, which are given in the appendix to Chap. VIII., have been kindly determined by Mr. A. B. Clark, at the laboratories of the Kodak Park Works, Rochester, New York, U.S.A.†

* And later editions.

† The indicators were not specially purified, but were of the quality usually employed in analytical chemistry. The instrument used was a Hufner spectrophotometer as described in "Investigations of the Theory of

(2) *Colorimetry.*—The object of colorimetry is to find how much coloured material is in a given solution, by adjusting the depth of a known solution so that light transmitted through it has exactly the same intensity as that transmitted through the unknown.

Since difference of concentration is balanced by difference in the thickness of the absorbing layer, it is clear that the validity of Beer's Law is presupposed (see p. 70), *i.e.*, it is assumed that within the limits of accuracy aimed at $C_0 l_0 = Cl$ in which C, $C_0$, $l$, $l_0$ are the concentrations and thicknesses of the two solutions. The method is therefore applicable to solutions such as $CuSO_4$, helianthin and I in $CS_2$, which undergo no change, or only a slight change in specific absorption with change of concentration.

The comparison may be carried out in Nessler tubes in which the depth of the standard solution is altered, or by means of a series of test-tubes in which the concentration is altered. In the latter case the observer looks across the test-tube. This relatively rough but quick and easy method is quite exact enough for many practical purposes.

In the colorimeter proper each half of the field of vision is illuminated by light which has passed through one of the two solutions. The disappearance of the line of demarcation between the two halves can be closely estimated.

The juxtaposition of the two fields may be effected by various devices. The light may be reflected on the two sides of a right-angled prism (Fig. 1). It is better that the reflecting surface of this should be of white matt rather than of polished glass. In the Donnan Colorimeter (*Zeitsch. phys. Chem.*, 19, 465 (1896)) the 45° mirror which reflects

the Photographic Process," by Sheppard and Mees. The indicators were placed in a Schultze cell having a 1 cm. layer, and the extinction coefficient determined by a visual matching of the two halves of the field. Compensating absorption filters were used to cut off scattered light. In the diagrams the ordinates are extinction coefficients for an absorbing layer 1 cm. thick, and the abscissæ wave-lengths in millionths of a millimetre.

light from the one solution is partly deprived of its silvering, and the light which has passed through the other solution and has been reflected from another mirror is seen through this transparent disc so formed.

The depth of the solution to be measured is usually kept to a fixed mark, while that of the standard solution is altered by means of a tap or reservoir of which the height can be adjusted. For further details the reader is referred to text-books of practical physical chemistry.

Sidgwick and Moore, *Zeitsch. phys. Chem.*, 58, 385 (1907), have found that colorimeter readings gain greatly in accuracy after a few days' practice. The personal factor remains large; readings of the two observers were found to bear a constant ratio to one another whether the absolute intensities of the colours measured were high or low. The ratio was in this case found to be $1{\cdot}07 \pm 0{\cdot}01$. Differences of the order of 10% between the results of different workers are therefore to be expected.

The comparison of change of intensity may be converted into one of change of tint by introducing light-filters of coloured solutions with or without gelatine between the source of light and the indicator solutions. Thus two blue solutions are furnished with yellow filters; any change in the intensity of the blue will produce a change in the tint of the green produced.

Quantitative colorimetry may be either used to determine rapidly the amount of coloured substances in solution, assuming the constancy of the absorption ratio, or if the absorption ratio is not constant, to determine the nature and extent of the deviation.

For further details on the theory and practice of colorimetry, the reader may consult: "Spekt. u. Col.," Baur, Bredig's Series, "Licht Absorption," Rudorff Ahrens', Sammlung IX., "Kolorimetrie," G. and H. Kruss, 1891, "Photo-chemistry," Sheppard, Longmans.

(3) *Spectrophotometry and the Extinction Coefficient.*— The specific light-absorbing power of a coloured solution may be more completely investigated by comparing the intensity of light of each wave-length which has passed through a given thickness of the solution with that of light which has not passed through the solution. The comparison is often made by introducing a block of glass into the cell containing the coloured liquid. The upper half of the slit is illuminated by light which has passed over the top of the glass block, *i.e.*, through the whole solution, the lower half by light which has passed through some solution and the block. If the latter is one centimetre thick the weakening of the light is that produced by one centimetre of solution.

According to another plan, the slit may be divided into two halves; before the one is placed the solvent, before the other the same thickness of the solution. The two rays of the given wave-length must then be increased or decreased in intensity to a known extent, *e.g.*, by adjustable slits, rotating Nicol's prisms, etc., until the two halves of the coloured field merge into one another. In the polarising type of spectrophotometer the rays pass through a dispersing prism and are polarised at right angles to one another. The intensities are then adjusted to equality by rotating an analysing Nicol's prism, and the angle is read. The positions of solvent and solution are then interchanged and the angle again read. If the intensities of the two rays are reduced from I to $I_1$ and $I_2$ by the solvent and solution respectively (I = intensity of incident light), then these intensities may be obtained from the tangents of the angles through which the analyser is rotated to produce uniform illumination in each case.

Then $\log 10 \frac{I_1}{I_2} = (K_2 - K_1)\, l$, $K_2$ and $K_1$ being the extinction coefficients (see p. 69) for the solution and solvent.

The extinction of the colourless solvent $K_1 l$ is small and is introduced to compensate for internal reflections, etc., and evidently includes the effects of that part of the absorption which is due to the solvent.

The theoretical definition of the extinction coefficient is founded on the general laws of light absorption. The intensity I for the comparison light of given wave-length which has only passed through the solvent, etc., is practically equal to that of the original light $I_0$.* The extinction coefficient $K_2$ obtained may therefore be taken as that of the substance in solution (K).

Then $$K = \frac{1}{l} \log \frac{I_0}{I}.$$

The extinction coefficient may evidently be defined as the reciprocal of that depth of solution for which $\log \frac{I_0}{I} = 1$, *i.e.*, of that depth which reduces the intensity of light to $\frac{1}{10}$ of its original value.

The first law of light absorption was stated by Lambert in 1760. Any small element of the thickness (or length) of a coloured solution of given concentration may be supposed to absorb a certain fraction of the light which passes through it. The next element will absorb the same fraction, and the rate of diminution of intensity in passing through each small element at each point is therefore proportional to the intensity I at that point. If $l$ is the length of each element, then

$$-\frac{dI}{dl} = K'I \quad \log \frac{I}{I_0} = -K'l,$$

and $$\frac{I}{I_0} = e^{-K'l},\dagger$$

* The extinction is usually measured of those wave-lengths for which the selective absorption of the coloured substance is considerable.

† K′ is variously called the absorption constant, absorption coefficient and absorption index.

or, using decimal logarithms,

$$\log_{10}\frac{I}{I_0} = -Kl \text{ and } \frac{I}{I_0} = 10^{-Kl}.$$

Extinction coefficients may refer to any concentration. The specific or molar extinction $\epsilon = K$ for unit C may also be defined when C is expressed in grams or mols. per unit volume respectively,

$$\log \frac{I}{I_0}/Cl = \epsilon.$$

The molar extinction will only be constant with variable concentration if the absorption of light is proportional to the number of mols. of the substance in solution irrespective of the volume in which the substance is contained, *i.e.*, if, when for two solutions $\frac{l_1}{l_2} = \frac{C_2}{C_1}$ then the total absorption of $l_1C_1$ is equal to that of $l_2C_2$ (Beer's Law). The specific or molar absorption $\epsilon$ in these cases may be defined for unit $lc$ and will be independent of concentration. Thus if Beer's Law is obeyed,

$$-\log\frac{I}{I_0} = KCl, \text{ or } \frac{I}{I_0} = \mu^{-Cl}$$

where $K = \log \mu$.

The concentration C divided by the extinction coefficient K or the reciprocal of the molar extinction is sometimes called the absorption ratio $= \frac{1}{\epsilon}$.

The constancy or otherwise of $\epsilon$ is a most important datum in the determination of complex formation or tautomeric change. Thus it has been shown by Hantzsch that Beer's Law holds for solutions of methyl orange between 0·0001 N. and 0·00002 N.

In solutions of varying [H·], however, the absorption ratio varies rapidly. The yellow solutions absorb blue

light more strongly than the red. The absorption ratio or molar extinction $\epsilon$ for the blue mercury line 436 (see p. 63) when $[H^{\cdot}] = 1{\cdot}2 \times 10^{-3}$ is only about one half the value of $\epsilon$ in completely alkaline solutions. If the limiting extinction of each form were known, the extent of the tautomeric change could thus be determined.

If it is found that for any light-absorbing compound Beer's Law holds, then one of two statements can be made:

(1) The relative amount of the coloured molecule is unaffected by dilution.

(2) Any other molecular species formed by a shift of equilibrium with dilution must possess, in the amounts formed, an absorbing power equal to that of the original molecule.

Thus, if the change is a dissociation

$$A_n = nA.$$

Then $n$ of A must absorb as much as 1 of $A_n$.

Now, in the theory of ionic colour as originally understood by some scientists, it was assumed that the colour, *e.g.*, of solutions of copper salts and permanganates was due to the ion only.*

If this were the case, the change of dissociation would result in a large divergence from Beer's Law, as may be seen by the following considerations. The given total concentration of a salt, for which the absorption ratio is defined will contain a lower proportion of ions at higher concentrations. The absorption ratio will therefore appear to be lower at these higher concentrations. But where it is possible to define independently the concentration of the coloured part the absorption ratio with respect to these will, on the above assumption, remain constant.

* Ostwald had investigated the absorption spectre of about 300 salts in dilute solutions and found that those of, *e.g.*, all permanganates and all rosaniline salts were identical. Since the ionisation is also nearly complete, the absorption in question was attributed to the common ion.

Thus, suppose for simplicity that the salt obeys Ostwald's dilution law, and let the concentration of the coloured ions be $C_1$.

Then

$$\frac{I}{I_o} = (\mu^{-c_i})l \quad \log \frac{I}{I_o} = -KC_i l$$

and the ionic absorption

$$-\frac{\log \frac{I}{I_o}}{C_i l} = \epsilon$$

is again constant.

The ionic concentration $C_i = \frac{K}{\epsilon}$ and also

$$\frac{C_i^2}{C - C_i} = K_D^* \therefore \frac{K^2}{\epsilon^2 C - \epsilon K} = K_D.$$

Since this function of K and C remains constant, then the function $\frac{K}{C}$, the molar absorption defined with respect to the total concentration does not remain constant. Now it was found by the earlier investigators that the absorption ratio did as a matter of fact vary with change of concentration, but the variation was only slight and not always in the same direction.

The results in the table are expressed as the absorption ratio, *i.e.*, $\frac{C}{K}$ or $\frac{1}{\epsilon}$

Magnanini showed that salts of copper and nickel and permanganates had the same colour after the addition of acids and bases which must have greatly altered the dissociation. The absorption spectra of copper sulphate, nitrate, and chloride are practically the same at concentrations below 0·003. The absorption of $CuCl_2$ does not

* The dissociation constant (see Chap. I.).

| Compound and Author. | Range of Concentration. | Mean $\frac{C}{K}\left(\frac{1}{\epsilon}\right)$. | Per cent. variation in $\frac{C}{K}$. | Direction of change of $\frac{C}{K}$ with dilution. |
|---|---|---|---|---|
| Vierordt $K_2 Cr_2 O_7$ | 0·0025 – 0·00031 | 0·00295 | 2 | increase |
| ,, $K_2 Cr O_4$ | 2·256 – 0·282 | 0·00188 | 3 | increase |
| ,, $Cr_2 (SO_4)_3$ (Chrome Alum) | 0·0718 – 0·0049 | 0·0455 | 2 | decrease |
| Sattegast $K_2 Cr O_4$ | 0·050 – 0·0067 | 0·07 | 3 | increase |
| ,, $K_2 Cr_2 O_7$ | 0·0025 – 0·0004 | 0·00365 | 3 | increase |

change under conditions of rapidly changing ionisation (Ewan, *Proc. Roy. Soc.*, 56, 57 (1894—5)). See also E. Muller, *Drude's Annalen*, (4) 12, 767 (1903); (4) 21, 518 (1906); B. E. Moore, *Phys. Zeitsch.*, 23, 321 (1906); P. Vaillant, *Ann. Chim. et Phys.*, 28, 213 (1903).

More recent researches, *e.g.*, those of Hantzsch and Hilscher, *Zeitsch. phys. Chem.*, 73, 362 (1910), and Bjerrum, *Zeitsch. anorg. Chem.*, 63, 146 (1909) have proved that in most cases of inorganic coloured salts the colour is to a considerable extent independent of the degree of ionisation. This has been particularly well shown in the case of chromic acid and its salts by Hantzsch, *loc. cit.*, and *Ber.*, 39, 4153 (1906); 41, 1216 and 4328 (1908); *Zeitsch. phys. Chem.*, 63, 367 (1903), although in some more recent work it appeared that the specific absorption of more concentrated solution of chromates does vary somewhat with the concentration, as well as with the nature of the alkali metal.

The extinction coefficient of the hexaquochrom salts was found by Bjerrum (*loc. cit.*, above) to be quite constant over a considerable range of concentration. The nature and

amount of the acid which was added to prevent hydrolysis also appears to have no effect on the extinction. The line of results quoted is for the wave-length 486 $\pm$ 6$\mu\mu$:

| Salt . . | $[Cr(aq)_6Cl_3]$ in 0·01 HCl | | | $[Cr(aq)_6](NO_3)_3$ in 0·1 $HNO_3$ | | | $[Cr(aq)_6](SO_4)_2^3$ in 0·2 $H_2SO_4$ | | |
|---|---|---|---|---|---|---|---|---|---|
| Mols. per litre . | 1 | 0·02 | 0·001 | 1 | 0·1 | 0·01 | 1 | 0·1 | 0·01 |
| Extinction Coefficient | 3·36 | 3·22 | 3·26 | 3·26 | 3·32 | 3·18 | 3·27 | 3·24 | 3·26 |

It was possible to be sure in this case that all the Cr was present as ions $Cr(aq)_6^{\cdot\cdot\cdot}$ or salt $Cr(aq)_6X_3$, since the formation of other complexes is slow and can easily be followed by the analytical estimation of the amount of anion. When this changes and the other complexes are formed, the colour of the solution and the extinction coefficient also changes.

In the case of copper sulphate not only is the absorption ratio nearly constant in solutions of the most different concentrations and degrees of dissociation, but this constancy also extends to the solid crystal hydrate. Plates of $CuSO_4$ $5H_2O$ were cut perpendicularly to the optical axis and polished. The molecular extinction was compared with that of acid $CuSO_4$ solutions.

Molecular extinction for—

| | $\lambda = \cdot 579\mu$ Yellow. | $\cdot 546\mu$ Green. | $\cdot 436\mu$ Blue. |
|---|---|---|---|
| Solid . . . | 4·75 | 2·07 | 0·381 |
| Solution . . . | 4·53 | 1·83 | 0·405 |

The experimental error is unavoidably large in the case of the solid, but the results distinctly suggest identity of absorbing power. The absorption is ascribed to the complex $Cu(H_2O)_4$ whether present as ion or sulphate. As soon as the $H_2O$ is replaced by $NH_3$, as in copper ammonia solutions, the

absorption changes its character. The molecular extinction curves at different concentrations of $H_2PtCl_6$, and $Na_2PtCl_6$ were found to fall almost together. For the blue Hg line $\lambda = \cdot 436\mu$ the molecular extinction only varies between $39\cdot2 - 41\cdot5$ in the case of three compounds of this type present at dilutions of $V = 10$ to $V = 500$. Here also then the absorption is to be ascribed to $PtCl_6$, not as ion only, however, but equally as compound. When an alteration in the nature of the complex is to be assumed on other grounds, there is an alteration in the colour, and the converse also holds (see Chap. III., Tautomeric Theory). Thus $CuCl_2 . 2H_2O$ is blue, $Cu(CuCl_4 . 2H_2O)$ is green. Abundant examples are furnished by the metal ammines. The change in the complex $(Co . 6NH_3)X_3$ to $(Co . 5NH_3 . H_2O)X_3$ results in a change from yellow to red.

The marked difference of colour between ferrous and ferric salts appears at first sight to point to an intimate connection between ionic charge and colour. The difference, however, may equally well be due to the formation of solvates, etc. The brown colour of $FeCl_3$ in water with no excess acid, similar to that of "dialysed iron" is due to hydrate formed by hydrolysis and in a colloidal condition; the pure yellow of acid solutions on analogy of Pt and Co salts, is probably due to an anionic complex. The case of Co salts is particularly instructive since still more marked changes of colour occur when there is no change of ionic valency. The pink colour is characteristic of cobaltous salts and ions. The blue of concentrated solutions or those containing much HCl is either due to decreased hydration or to the formation of ionic complexes. The direction of motion of the different coloured boundaries in an electric field has been investigated by Donnan, Bassett and Fox, *J. Chem. Soc.*, 81, 939—956 (1902). The colour of the $CoCl_2$ + HCl or alkaline chloride travels towards the anode

and is therefore probably characteristic of the complex anion $CoCl_3'$, while the normal pink colour of the cobalt ion travels towards the kathode. The probability that changes in the colour of other inorganic salts is due to complex formation and not ionisation is increased by these facts. Finally, it may be mentioned that the ultra-violet absorption spectrum of, *e.g.*, nitrates seems to show that there is no definite numerical relation between ultra-violet light absorption and degree of ionisation (Hartley, *J. Chem. Soc.*, 81, 556 (1902), 13, 221 (1903)); Schaefer, *Zeitsch. wiss Phot.*, 8, 212 (1910)).

The ultra-violet absorption of acetic acid is the same as that of acetates, although the degrees of ionisation are very different. On the other hand, there are undoubtedly some cases in which change of ionisation is quantitatively associated with change of colour. The ions $\dddot{Fe}$ and $CNS'$ have each only a slight colour, but the salt $Fe(CNS)_3$ a quite different and much stronger colour.

In the case of this deep red $Fe(CNS)_3$ solution Vierordt had found that the ratio $\frac{C}{\Lambda}$ increases with dilution. The colour is therefore probably due to the undissociated part. The observation of Gladstone that excess of either reagent deepens the colour leads to the same conclusion. If the colour is due to the undissociated salt, then the mixture of $x$ equivalents of $FeCl_3$ with $y$ of KCNS should give the same colour as that of $y$ of $FeCl_3$ with $x$ of KCNS, and it was shown by Magnanini that this was actually the case. Here also it is not impossible that it is not the gain or loss of a charge, but the labile nature of the valencies in the thiocyanate radicle which are responsible for the change. Ferric thiocyanate $Fe(CNS)_3$ may well have a different affinity distribution from $CNS'$.

The difficulty in finding a comprehensive explanation of

the colour of salts consists in the fact that the two possible causes—complex formation and combination of ions—are both favoured by increase of concentration. Each case must be judged separately on the evidence of quantitative absorption and the one or the other cause assigned according to the nature of this, combined with the evidence of conductivity, freezing-point, lowering, etc.

A survey of the data of light absorption has led Bjerrum to the conclusion that the ions of strong electrolytes have generally the same colour as the molecules even in concentrated solutions, provided that there is no formation of complexes, but that weak acids and bases and complexes have not the same colour as the ions. "We see that the primary products of combination of ions whose formation is governed by the Ostwald-Walden rule have the same colour as the ions, while those compounds which show anomalous dissociation and in which consequently the primary addition products have undergone further transformations possess quite a different appearance."

It was also said that the undissociated molecules of weak electrolytes usually have a pronounced tendency to form complexes with change of colour. Complex formation obviously implies a possibility of change of structure. Hantzsch, a little later, stated the opinion that "constitutively unaltered coloured acids produce not only ions of the same colour but also form salts of the same colour with colourless metal ions and esters of the same colour with alkyl and acyl radicles." The question as to how an alteration in constitution is to be recognised independently of the change of visible colour or of absorption spectrum leads to a short account of theories of colour in general, and in particular relation to some indicator types.

# CHAPTER III

## THEORIES OF COLOUR IN THEIR RELATION TO THE IONIC THEORY, CHEMICAL CONSTITUTION AND THE FORMATION OF SALTS

The general conditions and possible causes of colour change. The chemical structure theory. Colour changes in the solid state and in solution. The ionic theory of colour. Colour and tautomeric change. Nitroparaffins and ionisation isomerism. Nitrophenols and other nitro compounds. Benzoid and quinoid formulæ. The theory of "conjugation" by subsidiary valencies. Ionisation and tautomeric changes of the nitrophenols. Colour and salt formation in the case of organic bases. Acridine derivatives. Triphenyl methane derivatives—carbinol forms and true bases. Tautomeric changes of the phthalein indicators. Tautomeric changes of amino azo compounds.

### *The General Conditions and Possible Causes of Colour Change.*

The goal of all chemical explanations of colour is the complete correlation between change of colour and change in the structure of the molecule, using the word structure in its broadest sense to include the whole distribution of intramolecular forces as well as of the constituent atoms.

The conditions between which and the colour change a partial correlation has been established are:—

(1) Polymerism.

(2) Chemical structure as expressed by constitutional or graphical formulæ.

(3) Tautomerism, or the change of position of one or more atoms or atomic linkages on the same molecule without any permanent alteration of structure.

(4) Ionisation and salt formation, or change of electrical charge.

The difficulty of deciding which, if any, of these conditions is necessary and sufficient for change of colour lies in the probability that each of the conditions of the molecule implies one or several of the others, *e.g.*, polymerisation can hardly occur without some change in the distribution and affinity directions of the elements concerned. Thus $N_2O_4$ must have a different structure from $NO_2$.

The change of colour with change of molecular complexity may be illustrated by the examples of iodine vapour (purple to blue) and iodine in solution (brown or pink) (Beckmann, *Zeitsch. phys. Chem.*, 5, 76; Hantzsch and Vogt, *Zeitsch. phys. Chem.*, 38, 705).

Also ozone and oxygen (dark blue to light blue).

In many cases the colour darkens with decreasing molecular complexity and therefore with rise of temperature, since this usually increases the dissociation. Thus oxides darken on heating, sulphur is white at $-50°$, iodoform at $-70°$. The production of colour by the formation of complexes, *e.g.*, the red salt, $LiCl \cdot CuCl_2\,24H_2O$, from colourless, LiCl, and green, $CuCl_2\,24H_2O$, has been illustrated in the last chapter. Among organic dyestuffs in aqueous solution polymerism appears to be exceptional and not in itself a cause of colour. Thus methyl phenyl acridonium iodide has a molecular complexity of 5 in chloroform and forms simple molecules in pyridine. Yet it is deep red in both solvents.

A marked change of colour is often associated with those changes of physical properties, and in particular of crystalline form which are included under polymorphism. The red and yellow mercuric iodides are known as dimorphic forms of the same chemical individual, and without a deeper knowledge of the structures of the molecules which are responsible for the differences, it is sufficient perhaps to

state that polymorphism is a possible cause of change of colour in the solid state. A recent definition of polymorphism expressly excludes any ordinary changes of structure. "Substances are to be regarded as polymorphous provided that in no circumstances are properties exhibited by the different crystalline forms which are not explicable by a single formula" (*Chem. Soc. Ann. Reports*, VIII., 55 (1911)).

It is suggested in the account of polymorphism referred to, that the variety of colours exhibited by some solid organic compounds (polymorphic substances, chromoisomerides) is merely due to the production of polymorphic forms.

*The Chemical Structural Theory.*—In the original chemical theory of O. N. Witt certain groups of atoms were distinguished as chromophor or chromogen. It was stated that no coloured compound is without one or more of these groupings, which include :—

$$=C=C= \qquad C=O \qquad =C=NH \qquad -CH=N-$$
$$-N=N- \qquad \equiv C-NO \qquad -NO_2$$
$$=C=S$$

The presence of one of these although necessary is not always sufficient for the production of colour. Thus compounds of the type $R_2C=CR_2$ are colourless, but the multiplication of the chromogen gives the yellow hydrocarbon fulvene

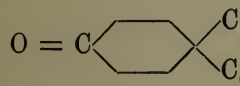
$$\begin{array}{l} CH=CH-CH \\ \quad | \qquad\quad || \\ CH=CH-CH. \end{array}$$

Benzophenone, $C_6H_5 \cdot CO \cdot C_6H_5$, with another chromophore becomes yellow benzil, $C_6H_5 \cdot CO \cdot CO \cdot C_6H_5$. The group $=CS$ is a stronger or independent chromophore, and $C_6H_5 \cdot CS \cdot C_6H_5$ is blue without further substitution.

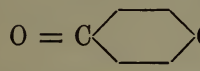
The azo group is a still stronger chromophore, and the simplest carbon compound containing this group,

is already yellow.

The substitution of hydrogen by "auxo-chrome" groups makes the colour more intense and moves it towards the red. The groups $NH_2$, OH, etc., are called "batho-chromic," since they deepen the colour. The opposite or hypso-chromic effect of lightening the colour is noticed when any of these groups are replaced by hydrogen, or when some are replaced by others. A batho-chromic effect is the production of orange aurin—




from yellow quinone




The auxo-chromic powers of $CH_3$, $C_6H_5$, OH and $NH_2$ may be illustrated by some of the compounds which are used as indicators, best perhaps by the magenta group. Thus the substitution of $CH_3$ for H in the amido groups of rosaniline salts changes the colour from yellow to violet (crystal violet). The group $C_6H_5$, when substituted for three amino hydrogens, produces the blue tri-phenyl-rosaniline chloride, $(C_6H_4 \cdot NHC_6H_5)_2 : C : C_6H_4 \cdot NHC_6H_5Cl$.

The replacement of the $NH_2$ groups by OH changes the colour back to yellow (rosolic acid).

Selective absorption of light begins in the ultra-violet. Compounds such as benzene or acetyl acetone, $CH\,CO \cdot CH_2 \cdot CO \cdot CH_3$, show well-marked bands in this region. No visible colour is produced, since obviously the complementary or residual light which is transmitted contains the

whole of the visible spectrum. With the introduction of auxo-chrome groups the absorption bands move into the violet and the complementary colour, greenish yellow, appears. Thus para-nitro-aniline, $C_6H_4[\overset{1}{N}O_2][\overset{4}{N}H_2]$, and diacetyl, $CH_3 \cdot CO \cdot CO \cdot CH_3$, are yellow.

Complementary pairs of colours are :—

| | | | | |
|---|---|---|---|---|
| violet | indigo | bright blue | blue green | green |
| green-yellow. | yellow. | orange. | red. | purple. |

As the absorption bands move along the upper series from left to right, the visible colour moves along the lower series in the same direction (Nietzki, 1899). With increasing batho-chromic substitution the colour might continue to move now along the upper series, but before this complete course can be traversed other bands have usually appeared from the violet end. This theory is a useful aid in the classification of dyestuffs and a guide to the synthesis of new compounds. It affirms a causal connection between certain constitutions and colour, but leaves open the question as to the structural changes to which the effectiveness of the chromophore, etc., groups are due. The changes of colour undergone by the same indicator in different solvents, and especially in solutions of varying $[H^{\cdot}]$, demands a more precise theory of the connection between light absorption and the vibrations of atoms or valency lines of force.

No definite auxo-chrome effect can be ascribed to the gain or loss of an electron, although many colourless substances, *e.g.*, phenolphthalein, tri-phenyl amido methane bases give coloured salts. On the other hand, the nitranilines are yellow and the salts colourless. The colour of the sodium salt of helianthin is much less intense than that of the uncharged or amphoteric molecule. In what follows, each theory is used so far as it gives a serviceable

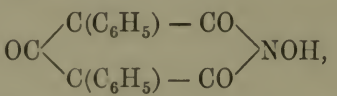
picture of the facts which are included in the subject. The great variety of colour displayed by substances such as violurates, acridonium compounds, etc., under the influence of slight changes of solvent, substitution, temperature and light is somewhat beyond the scope of the present work. These changes, known as chromoisomerism, thermotropy, phototropy, etc., no doubt correspond to very fine adjustments of vibrations within the molecule, and will have to be accounted for in a comprehensive theory of colour. It is, however, not yet proved that even these polychromic changes are inconsistent with the simpler provisional theories described below, since many of the intermediate colours have been explained as being due to equilibria between a few forms in liquid or solid solution. The greater simplicity of the colour changes in aqueous solution may be expressed by the idea that the solvent has an equilibrating effect upon the highly variable valency systems which may be formed between the acid and the basic affinity centres of the solid compounds, *e.g.*, the violet, blue, yellow-orange and red solid violurates of the alkali metals, which all tend to revert to the same blue colour at high dilutions in water.

According to Baly the affinities of the atoms, which are left over when the molecule is formed, neutralise one another as far as possible. The self-neutralised affinities on the molecule may be opened up by light, or the residual affinity of the solvent. Solvents of an unsaturated character with high residual affinity are particularly effective. An increase in the residual affinity of the solvent displaces the absorption band towards the red (Baly, Tuck and Marsden, *J. Chem. Soc.*, 571 (1910)).

At high dilutions the absorption spectra of substances in solution approach more closely to those of the same compounds in the state of vapour. The absorption is in both

cases that of the molecule freely oscillating according to its structure, and with no constraints and no closed fields of forces due to the formation of solvates, polymers, solid solutions. The simplest spectra of azo and amino azobenzenes have been thus investigated by Purvis, *J. Chem. Soc.*, 105, 106, 590 (1914).

The power of resolving the closed molecular fields of force appears to vary considerably, both with the residual affinity of the solvent itself, and with the nature of the affinity centres which are opened by solution. Thus the lithium salt of diphenyl violuric acid,

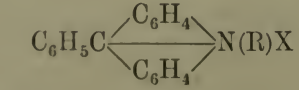


which may be red or yellow with the solid state, dissolves with the following colours,

| water (dilute). | water (concentrated). | methyl alcohol. | phenol. | chloro-form. | acetone. | pyridine. |
|---|---|---|---|---|---|---|
| violet. | red-violet. | red. | orange. | red-orange. | red. | violet. |

(Hantzsch and Robison, *Ber.* 43 (1), 45 (1910); Hantzsch and Heilbron, *Ber.* 43 (1), 68 (1910)).

The intensity of the colour of the alkyl acridonium salts



in the solvents, water ——› ethyl alcohol ——› anyl alcohol ——› chloroform increase in the order given.

The absorption of light is often weaker and further removed towards the region of shorter wave-lengths in hydroxylic solvents, and especially water. In these it may be considered that the lines of force of the solute molecule are most completely opened up, with subsequent ionisation

if any group is present which has a pronounced electro affinity. The general effect of solvents upon light absorption has been stated by Baly and Tryhorn, *J. Chem. Soc.*, 107, July, 1915.*

"On addition of solvent to a substance exhibiting selective absorption, the absorption band shifts at first towards the red until a minimum value of the central frequency is obtained, the concentration at which this occurs depending upon the relation between the affinities of solute and solvent. Further dilution causes a progressive shift of the absorption towards the shorter wave-length until at great dilution a constant maximum frequency is reached. This maximum frequency is the same as that exhibited by the absorbing substance in the state of vapour."

### *The Ionic Theory of Colour.*

In its simplest form this theory asserts that the colours of organic compounds, as those of inorganic salts are primarily determined by their state of electrolytic dissociation. Ostwald defined an indicator as an acid or base which possesses different colours in the ionic and in the electrically neutral or undissociated condition. Thus the sodium potassium or barium salts of phenolphthalein owe their characteristic colour to the ion, the free acid being colourless. Since according to the evidence of conductivity and according to their constitution indicators generally belong to the class of weak acids or bases, *i.e.*, to those which are only slightly dissociated at ordinary concentrations, it is clear that the relative amounts of ions and neutral molecules must vary greatly in passing from the compound to

* See also Baly and Hampson, *J. Chem. Soc.*, 107, 248 (1915), and preceding papers, and Baly and Tryhorn, *Phil. Mag.* (vi.) 31, 185, p. 417, May, 1916.

its salts. From the examples already given of the operation of chemical equilibrium in electrolytes, it is clear that when NaOH is added to HCl containing a little $CH_3 \cdot COOH$, the slightest excess of alkali beyond that equivalent to the HCl will greatly alter the amount of acetyl ion. If for the acetic acid is substituted a coloured acid this change will become visible as a turning point of colour.

If the turning point of the indicator is far on the acid side of the neutral point, it may be said either that it is a moderately strong acid, and therefore requires a high $[H^{\cdot}]$ to convert an appreciable fraction into the uncharged condition, or that it is a very weak base, and requires a high $[H^{\cdot}]$ to diminish the hydrolysis of the salt and produce an appreciable fraction of ion. Similar explanations are found for indicators changing on the alkaline side, and are supported by what is known of the chemical constitution of the indicator. The principal support of the ionic theory of indicators is the fact that in some cases the colour changes appear to result from the operation of the dilution law and that the apparent dissociation constant found by the colorimetric method agrees with that found by conductivity.

Violuric acid is a particularly striking example of this agreement, and is also of interest as having been cited by Magnanini as an example which disproved the ionic theory. The specific colour violet was said to be characteristic of the ion since it was well developed in solutions of the alkali salts and also, though to a less degree, in the free acid. A solution of violuric acid was, however, prepared by Magnanini, which remained colourless at a dilution of 1 mol. in 250 litres, at which it was, as shown by the conductivity, dissociated to the extent of 8 per cent. The salts gave violet aqueous solutions, the specific colour of which was not altered by dilution or by the addition of $KNO_3$,

both of which should have altered the ionisation. For it will be recalled (see p. 72) that the specific colour if referred to the ions should increase continually as dilution proceeds.

These difficulties were partly elucidated by the work of Wagner, *Zeitsch. phys. Chem.*, 12, 314 (1893), and Donnan, *Zeitsch. phys. Chem.*, 19, 465.

Violuric acid was found to be in fact one of the best examples of a quantitative correspondence between colour and conductivity, for the intensity of the colour could be directly calculated from the degree of ionisation and *vice versâ*. Thus it was shown that the intensity of the colour was halved by diluting a solution from V = 40 to V = 160. By this means the total concentration is, of course, quartered, but the ionic concentration is halved.

It was further shown that the changes of colour of this acid in the presence of others could be calculated by the principles of isohydry from its dissociation constant $K = 0{\cdot}0_4272$. When the solution was made $0{\cdot}0_34N$ with respect to HCl the degree of dissociation of the violuric acid was reduced from 4·08 to 3·03 per cent. The degree of dissociation found colorimetrically was 3·10 per cent. Also on the addition of an acid of nearly the same dissociation constant (p. oxybenzoic acid $K = 0{\cdot}0_4286$) the calculated reduction in the dissociation of the violuric agreed with that found colorimetrically. It appeared altogether from the results that the free acid was colourless and the ion violet, but that the undissociated salts were also violet. Thus the colour of this compound is an effect of salt formation and not merely of ionisation. A further account of this acid is given above (see p. 84).

The advantage of the ionic theory consists in this, that by its aid a quantitative account of the phenomena can be given, and indicators can be classified according to a practically useful scheme. But the reasons why it can

never by itself form a comprehensive and satisfactory theory may be summarised as follows.

In most of the cases which had been given as examples of ionic colour it has been shown that the specific light absorption is characteristic of the salt and not merely of the ion (see also Chap. II.).

The change of colour brought about by change of solvent sometimes far exceeds any possible change of ionisation from this cause. The effect of adding organic solvents such as methyl and ethyl alcohols does not bear a simple relation to their ionising power (see section on the effect of alcohol, etc.).

The great variety in the colour of solid indicator salts when certain molecular linkages are present and the simplicity of colour when these are absent makes it necessary to assume a causal connection between change of structure and change of colour. All indicators contain one or more of these linkages which are known on grounds to undergo tautomeric change.

Some indicators undergo a whole series of colour changes in solutions of varying [H·] (see pp. 159, 160). This could only be explained on the ionic theory by progressive ionisation of a more complicated type than is possible from the number of acid or basic affinity centres. But the possibilities of tautomeric change between the affinities of these centres are more numerous.

The fact that some indicator changes require a measurable time for completion (see p. 154) shows that in these cases there are certainly other reactions involved besides those between the ions. Several examples of such time reactions, amongst the nitro-paraffins, etc., are given below. That they are not more common among indicators is simply due to the fact that indicators are selected because their changes of colour are practically instan-

taneous. Several examples of gradual fading or recovery of colour however, are mentioned below, notably in the amido triphenyl-methane group.

*Colour and Tautomeric Change.*

The theory that change of colour is always due to a change of constitution was put forward by Bernthsen, *Chem. Zeit.* (1892), and Friedlander, *Ber.*, 26, 172 (1893), independently in 1892—1893 in order to explain the behaviour of phenolphthalein.* An historical account of the ionic and tautomeric views is given by Margosches, *Zeits. angew. Chem.*, 20, 181 (1907). The chemical, theory of colour, as it has been called, requires the establishment of two propositions.

(1) All changes of colour must be shown (by independent evidence) to be accompanied by changes of constitution.

(2) In cases where the constitution is known to be unaltered there must be no change of colour.

The probability that the formation of salts may bring about a change of structure is strengthened by the evidence that in some cases such changes must be postulated in order to represent in a satisfactory manner the constitution of the salts which are formed. The nitro-paraffins $R{\cdot}NO_2$ cannot, according to this structure, give an acidic hydrogen. And, in fact, nitro-methane $CH_3 \cdot NO_2$ has normally no acid reaction, and its solution in water has only a very low conductivity. When, however, it is kept in contact with $Ba(OH)_2$ solution, the conductivity of the system falls, showing that a barium salt is being formed. Nitro-methane in aqueous solution may also be titrated as a monacid base with HCl in the presence of methyl orange. It is natural, therefore,

* The benzoid quinoid structure for the coloured and colourless nitrophenols had been previously proposed by Armstrong (p. 95).

to assume that the compound in aqueous solution possesses potentially a structure $H_2C:NO\cdot OH$, which would allow it to ionise as an acid. The difference between the free nitro body and its salts is shown qualitatively in this case by the red colour which the latter, but not the former, gives with $FeCl_3$.

These changes are typical of many others which a whole series of compounds, in particular those containing $NO_2$ and $NH_2$ groups, undergo when treated with alkalies or acids in aqueous solution. As will be clear from the examples given below, there is a high probability that in all the cases investigated the actual cause of the change of colour is a change of structure, or "ionisation isomerism," which is favoured by the same causes that bring about ionisation.

*Nitro-Paraffins and the Criteria of Ionisation Isomerism.*

It is possible in the series of nitro-paraffins to distinguish one form which by its constitution and properties is a non-electrolyte, true nitro-body, normal form, or pseudo acid, and another form which gives salts, etc., and is called an iso-nitro-body or aci-compound. In some cases the free aci-compound can be isolated, but the tendency to pass into this form appears to vary greatly even in closely allied compounds. Thus dinitro-methane is strongly acid in aqueous solution, dinitro-ethane only slightly so. A variety of phenomena are possible according to the conditions of equilibrium between the two forms. When nitro-ethane $C_2H_5NO_2$ is dissolved in water and an equivalent of NaOH is added, the neutralisation is not instantaneous as in the case of an ionic reaction. The rate of reaction (which can be followed by the change of conductivity) is governed by the rate of transformation. The hydrogen atom on the

normal molecule does not occupy the same position as the sodium in the aci-molecule.

The re-arrangement $CH_3 \cdot CH_2 \cdot NO_2 \longrightarrow CH_3 \cdot CH : N\overset{O}{\underset{OH}{<}}$

must first take place before the neutralisation can proceed. When the sodium salt is treated with an acid, the first product should be the iso-nitro-compound

$$CH_3 \cdot CH : N\overset{O}{\underset{Na}{<}} + HCl = CH_3 \cdot CH : N\overset{O}{\underset{OH}{<}} + NaCl.$$

The existence of this compound is rendered probable by the fact that the conductivity is at first considerably greater than that of the NaCl formed, and sinks to this value in a few days at 0°, in a few minutes at 25°.

Time is also required for the production of pseudo form in the case of phenyl nitro-methane $CH_2(C_6H_5)NO_2$. The sodium salt when treated with acid gives at first the solid aci-compound which gradually passes into the liquid pseudo-compound. The greater slowness with which the stable configuration is produced in this case may be due to steric hindrance. If the neutral non-electrolyte form of the compound is that commonly known, and is therefore stable under ordinary conditions, then the prefixes aci- or baso- are used for the electrolyte forms. If the acidic or basic form can be easily prepared in the free state, or if the compound is commonly known in the form of its salts, then the prefix pseudo is used for the neutral form.

The criteria for the existence of ionisation isomers have been systematically stated by Hantzsch and are mainly founded on the results of his co-workers (*Ber.* 32 to 40 (1899 to 1907)). The first criterion follows from the preceding examples.

(1) If the neutralisation of a hydrogen compound is a time reaction, then the compound is a pseudo acid (base). The converse of this is not necessarily true. The neutralisation may appear to take place instantaneously, because the tautomeric transformation is itself rapid. Thus dinitro-ethane is formed instantaneously from its sodium salt at 0°. No tautomeric change is therefore to be postulated on this account, yet the free substance has almost certainly the constitution $CH_3CH\begin{cases}NO_2\\NO_2\end{cases}$, and the sodium salt by analogy with the strongly acid dinitro-methane has the aci-constitution. Thus an instantaneous reaction is not necessarily only an ionic one, since in these cases by analogy and by the proofs given below there is reason to believe that a tautomeric change is involved. If this is the case it may sometimes be detected by the fact that a very slight change of conditions alters the velocity in a high ratio. Thus it has been shown by Biddle * that the velocity of change of colour in the aminotriphenyl methane group is highly dependent upon the [H·] of the solution.

When the neutralisation is instantaneous under the usual conditions, the tautomerism can still be proved by another line of reasoning. The free compound dinitro-ethane forms a solution which practically does not conduct the electric current. If an acid at all, it must therefore be an exceedingly weak one. But the sodium salt reacts neutral as if it were the salt of a strong acid. It cannot therefore have the constitution $CH_3 \cdot CNa\ (NO)_2$ which, being derived from a very weak acid, would be more strongly hydrolysed than, *e.g.*, KCN. The second criterion of tautomerism may then be stated.

* *J. Amer. Chem. Soc.*, January, 1914.

(2) When compounds which in the free state form non-conducting or only slightly conducting aqueous solutions also form salts with strong bases (acids) which react nearly neutral, then the compounds are pseudo acids (bases).

Ethyl nitrolic acid dissolves in water to form a colourless solution with a very small conductivity. It gives alkaline salts which have a neutral reaction $CH_3 \cdot C(NO_2) : N \cdot ONa$. It is therefore a pseudo acid. The salts are red, and therefore change of colour is here associated with change of constitution. There is another colourless series of salts, but these also are optically, as well as chemically, different from the free compound (*Ber.*, 32 (1899), 42 (1909); and Hantzsch, Hantzsch and Kanasirski). A third criterion of tautomerism may then be stated.

(3) If a compound, colourless in the pure state, in non-aqueous solvents and (sometimes) in water, gives coloured ions and solid salts (with colourless kathions and anions of course), then it is a pseudo acid (base).

Another sample example of this colour change is nitro-form. The pure compound and its solutions in non-aqueous solvents are colourless, and it is in these considered to be the true tri-nitro-methane.* It dissolves in water to form a yellowish solution and gives a series of salts which are yellow both in solution and in the solid state. The compound therefore exists in a neutral and an aci-form. There are, however, two mercury derivatives of nitro-form, one yellow, which is naturally supposed to be derived from the aci-form like the other salts, and one colourless in which the mercury is probably united directly to the carbon atom and which is derived from the true tri-nitro-methane. The proof is hereby made more complete since it is known that mercury has a tendency to be substituted for hydrogen in

* Compare, however, the coloured iodoform.

such a position, producing a compound which is not a true salt.*

The converse of proposition (3) is not necessarily true. A colourless pseudo acid may give a colourless aqueous solution because the velocity of transformation is too slow, or because the aci-form itself is only a weak acid.

Or the salts may be colourless because the aci-form itself has no visible colour. Thus the nitro-ketones give a colourless as well as a coloured series of salts, but the former, as well as the latter, are both optically and chemically different from the pure compound, and being true salts must necessarily be derived from an aci-form.

With these apparent anomalies in the phenomena of neutralisation and hydrolysis is often associated an unusually high temperature coefficient of conductivity. The increase of conductivity of dinitro-methane, paranitrophenol, violuric acid and similar compounds is sometimes as much as 100 per cent. for a moderate rise of temperature. Since the temperature coefficients of ionic mobilities do not exceed certain limits (see p. 10), the increase of conductivity must be attributed mainly to an increase in dissociation, or in the amount of aci-form present. The dissociation constant of violuric acid increases $2\frac{1}{2}$ times, and that of oxazolone 7 times between 0° and 35°, while that of laevulinic acid only increases by 5 per cent. in the same interval.

(4) A fourth criterion of tautomeric change is then to be found in an abnormally high increase in the dissociation constant with temperature.

The shift of the equilibrium towards the coloured aci-form with rise of temperature is clearly shown by a deepening colour, *e.g.*, the yellow or violet of the compounds

* Mercury nitro-form has an absorption spectrum resembling that of the potassium compound when dissolved in water; but in chloroform solution it absorbs light in the same way as nitro-form itself

$$(NO_2)_2C = NO_2\,hg \longrightarrow (NO_2)_3 \equiv C - hg.$$

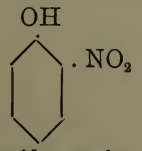
mentioned above. The change is reversible, for the colour returns to its original paler tint on cooling.

The theory of tautomeric change as deduced from the nitro-paraffins appears in its simplest form, but similar theories can be advanced to account for the colour changes of the nitro-phenols and other types of the compounds used as indicators, in which the possibilities of position and valency isomerism are more numerous. In the absence of a comprehensive theory, it is best to give some account of each type separately.

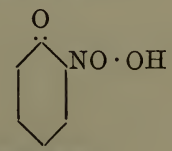
*Nitro-phenols and other Nitro-Compounds.*

In the case of the aromatic, as in that of the aliphatic nitro-compounds, the salts appear to be derived from an acid, which is much stronger than is probable from the constitution of the normal compound. Phenol itself is an exceedingly weak acid (see p. 37) and the chloro-phenols are also weak. Thus the dissociation constant of trichloro-phenol is only $2{\cdot}8 \times 10^{-8}$ (Walker, *Zeitsch. phys. Chem.*, 32, 137 (1900)).

Therefore the substitution of negative radicles has in itself only an insignificant effect upon the dissociation constant. Yet the mono-nitro-phenols are moderately strong, and tri-nitro-phenol a very strong acid. The hydrogen atom which is transferred to the $NO_2$ group in order to produce these strong acids is probably derived from the phenolic hydroxyl. The structural ortho-nitro-phenol formulæ which express this change were first suggested by Armstrong (see *Proc. Chem. Soc.*, 1888 to 1896).



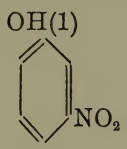

Benzoid neutral.



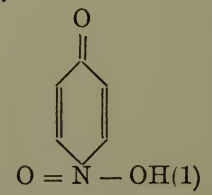

Quinoid aci-.

The yellow salts are derived from the quinoid aci-form, while the parent compounds, which are colourless or weakly coloured, and the normal ethers which are colourless, exist predominantly in the pseudo acid, phenolic or benzoid form.

Paranitro-phenol.




Alkyl or acyl groups may be substituted in position (1), giving ethers or acyl compounds.




Metals may be substituted in position (1), giving salts.

In addition to the usual colourless ethers a coloured series has been prepared ; these are, however, red and not yellow like the usual salts.

Many of the salts are, however, red or orange, and others can be prepared in both red and yellow forms. Also red ethers are known, such as that of tri-nitro-phenol. The yellow and red forms seem to be closely allied and the difference between the solids vanishes in solution, *e.g.*, the red ortho-nitro-phenol ester and the yellow potassium salt dissolved in alcohol have almost identical colours and absorption spectra. This and other evidence which is to be found chiefly in the papers of Hantzsch and co-workers (1906—1909) justifies the belief that the red and yellow form are both derived from the aci- or quinoid molecule. The coloured ethers are therefore esters. While the preparation of a series of yellow ethers and colourless salts would no doubt complete the parallel in a satisfactory manner, yet their non-existence in many cases can be accounted for by a high degree of instability. The red esters are themselves metastable with respect to the

colourless ethers, and can only be prepared because their rate of transformation is low.

The stability or otherwise of the colourless forms may also be predicted from the constitution.

(1) When the hydrogen atom is substituted by an organic radicle, the resulting colourless compound is the stable one under all conditions.

(2) On the other hand, the attachment of the original hydrogen atom or an electro-positive metal to the affinity centre which produces the tautomerism, gives in general a compound which is not fixed in one or the other form but is in a state of incomplete equilibrium, both forms being present in proportions which vary with the temperature, nature of the solvent, etc.

(1) As examples of derivatives which cannot pass into the quinoid structure, may be taken the colourless ethers, also tri-nitro-benzoic acid, tri-nitro-phenol acetate (from dry silver picrate and ethereal acetyl chloride), and ortho-nitro-phenol acetate. These compounds are not only colourless to the eye, but also optically colourless; they show no selective absorption. Their optical nature is unaffected by changes of solvent and temperature and appears to depend upon the impossibility of spontaneous tautomeric change. Tri-nitro-phenol acetate and other compounds of this nature are indeed turned to a strong yellow by a trace of water, but this change is, of course, to be attributed simply to hydrolysis.

(2) The fractions of the original hydroxy compounds transformed under different conditions vary widely. The colours of the solid compounds may be due to a true equilibrium percentage of the coloured form, or perhaps to a fairly constant trace of solvent or other impurity always included in the ordinary pure product. Many nitro-compounds, usually yellow, may be obtained in a colourless

state by special precautions. Thus a colourless specimen of nitro-benzene may be prepared by repeated fractional crystallisation, but it becomes faintly yellow on standing. Nitro-naphthalene may be decolourised by recrystallisation from alcohol in the presence of animal charcoal. Meta-nitro-phenol is also almost colourless when carefully re-crystallised, but ortho-nitro-phenol is persistently pale yellow. The amount of coloured compound present in solid ortho-nitro-phenol and picric acid has been roughly estimated by Hantzsch. The colour was matched against a mixture of the respective potassium salts (assumed fully quinoid) mixed with a colourless solid ($BaSO_4$). The amount of coloured compound is thus estimated at about 1 per cent. for ortho- and less for tri-nitro-phenol.*

Picric acid has been prepared colourless by Marckwald, *Ber.*, 33, 1128 (1900). This preparation, however, is not optically colourless but absorbs ultraviolet light selectively, as do also the colourless solutions of the nitro-phenols in organic solvents and the vapour of ortho-nitro-phenol at 300°.

The colour of nitro-phenols varies with the solvent in the following order :—

Chloroform, benzene, ether, alcohol, water,
colourless, weak absorption in ultraviolet ⟶ yellow.

This order, although usual, is not always preserved. Thus para-nitro-phenol is colourless in most organic solvents and in water, but slightly yellow in alcohol (decidedly in pyridine).

The progressive shift in the tautomeric equilibrium can have nothing to do with ionisation in the first three solvents. Temperature also affects the colour, and in such a way that this usually deepens on heating in the case both of the

* Since the two solid forms cannot exist side by side in equilibrium, they must be in a state of solid solution, or the velocity of transformation must be low.

solutions and of the solids. The increase of colour may be due to an alteration in the equilibrium amounts of yellow and red aci-form, since the deepening is observed also in the case of the alkali salts which are practically all in the quinoid form already.

By the work on which the preceding summary is based the probability of the following changes has been established:—

(1) A constitutional change.

$$\text{Benzoid} \rightleftharpoons \text{quinoid}$$

$$\text{Colourless} \rightleftharpoons \text{coloured.}$$

Favoured by salt formation, dissociating solvents, and perhaps rise of temperature.

(2) A change.

$$\text{Quinoid yellow} \rightleftharpoons \text{quinoid red.}$$

(3) The ionisation of the quinoid forms (acid or salts) in dissociating solvents.

Each of these equilibria could no doubt be expressed by constants, the relative magnitude of which will be influenced:—

(*a*) By the nature of the solvent and physical conditions as exemplified above.

(*b*) By the number and position of the substituting groups.

The intensity of colour in the compounds when solid and when dissolved in indifferent solvents decreases on the whole in the order:—

Ortho-mono-, tri-, 2, 4 di-, meta-mono-, and para-mono-nitro-phenols.

The order of the alkali salts is different, the intensity of colour being greatest with tri-, and least with ortho-nitro-phenol. The free compound ortho-nitro-phenol is more yellow and has a higher transformation ratio aci/pseudo

than tri-nitro-phenol. So also nitro-benzene is pale yellow and tri-nitro-benzene colourless. In the salts, on the other hand, the multiplication of nitro groups raises the transformation ratio and the ionisation to a marked extent. The di-nitro-phenols are stronger acids than the mono-, and the tri- are stronger than either. So, also, nitro-benzene does not give coloured solutions with alkali, but tri-nitro-benzene has weakly acid properties and gives a reddish brown solution with a slight excess of alkali.

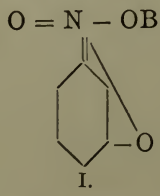
*Meta-nitro-phenols.*

If the explanation of tautomeric change is to centre round the benzoid, quinoid structures, it must be noted that meta-nitro-phenols do not differ essentially in their colour changes from the other isomers. Meta-nitro-phenol is yellow as usually prepared, but may be obtained nearly colourless. It gives a yellow solution in water which is made colourless by a little HCl.

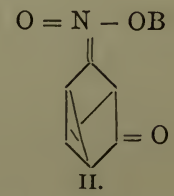
Colourless and coloured ethers, and yellow, orange and red salts are known. From the orange solutions of an alkali salt * there have been prepared small yields of yellow and red by the evaporation of alcoholic solutions free from water (Hantzsch, Rosanoff, *Ber.*, 40, I., 331 and 332 (1907)).

The aci-form of the meta-compound could be represented by formulae which though not in accord with common usage are not in themselves impossible.

Formula II. is analogous to the quinoid.




I.



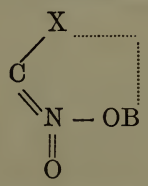

II.

* The potassium salt of tri-bromo 3, 5, di-nitro-phenol.

The ring structure I. was proposed by Hantzsch to account for the yellow and red salts as syn- and anti-forms. If used, it would naturally be applied also to the ortho- and para-compounds. But there is little independent evidence of any correlation between geometrical isomerism and colour. In any case the disposition of the valencies of the benzene nucleus is not the most important question here, since the really necessary condition is the presence of the unsaturated groups. The benzene nucleus may be loaded in many ways, as in the bromo-nitro-phenols and tetra bromo-phenol phthalein, without materially affecting the colours, which are also developed in the open chain series.

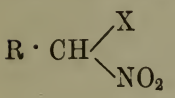
The exact mode of interaction of the affinity centres which produce colour is a field for hypothesis. In the conjugation theory it is supposed that a closed ring is formed which permits oscillations either of "labile" atoms or valencies.

*The Conjugation Theory.*—This generalisation was stated in a paper by Hantzsch and Voigt, *Ber.*, I., 45, 85 (1912). The production of colour is due to conjugation, or the formation of an auxiliary valency bond (represented by . . . . .) between the hydrogen or substituting metal and a neighbouring radicle, which may be $NO_2$, NOH, CO, COOH, $COOC_2H_5$, $CONH_2$, CN, or $C_6H_5$. The closed chain thus produced may be represented by



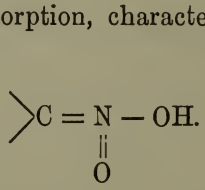

A study of the absorption spectra of compounds containing the above-mentioned groups, *e.g.*, nitro-paraffins, nitro-malonic esters, nitro-aliphatic acids, nitro-ketones, shows that these belong to three main types.

(1) There is an absorption band or alteration in the direction of the absorption curve at about $1/\lambda = 3{,}413$. This is characteristic of the true nitro-compounds



in which X may be $NO_2$, NOH, RCO,* COOH, $COOC_2H_5$, $CONH_2$, CN, $C_6H_5$, without altering the general character of the absorption. A similar absorption is found in the case of acetone, and the di-alkyl aceto-acetic esters.

(2) A general absorption, characteristic of the simple aci-nitro-compounds.

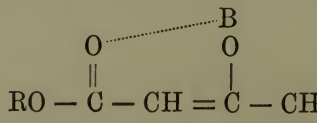


This type is only known in the salts of the mono-nitro-paraffins.

(3) A strong selective absorption characteristic of aci-nitro-compounds in which there is a second substituent X which may be any one of the list given above.

When these compounds can be prepared in the pseudo-form, the absorption returns to (1).

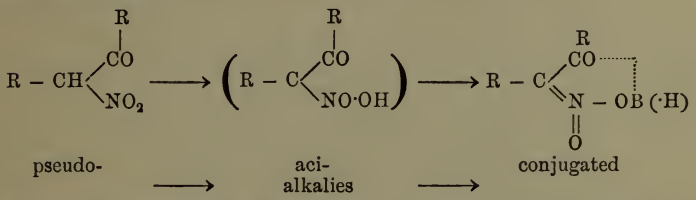
Salts of aceto-acetic ester and di-ketones have a similar absorption and their structure can be similarly represented.



When the conjugation is possible, as in the case of the di-nitro-paraffins, nitro-phenols, etc., it always takes place

* CO in original paper.

and the absorption appears to pass straight from type (1) to type (3), the aci-compound if formed at all having a very high velocity of transformation. Thus, in the case of the nitro-ketones :—




Most organic solvents contain principally the neutral or pseudo-form, dissociating solvents produce greater or less amounts of the conjugated forms, but water is the only neutral solvent which is able to produce this change in some nitro-compounds, *e.g.*, di- and tri-methane. An increase of temperature also appears to favour form 3. In some cases the salts as well as the acids appear colourless (see p. 93), but an examination of the absorption spectra shows that the typical conjugation bands are present in the ultraviolet.

There is no direct proportionality between colour and ionisation, for 0·0001 N. solutions of di-nitro-methane and its potassium salt are optically identical, while the degree of dissociation of the acid according to its constant = 0·000268 is 75 per cent. and that of the salt is practically complete. On the whole, then, it is supposed that the conjugated structure is always brought about by the attachment of strongly electro negative (or positive, see next section) substituents to certain affinity centres. This structure invariably causes visible or ultraviolet colour. Ionisation is a natural consequence of the high electro-affinity of the substituents, but not a cause of the colour. For a criticism and discussion, see Harper and Macbeth, *J. Chem. Soc.*, 107 and 108, 87 (1915).

*Ionisation of the Nitro-phenols.*

The constant of transformation aci/pseudo may have the most various values and each of these may be combined with different values of the dissociation constant. There must always be some undissociated aci-form present, and this may require a large amount of undissociated pseudo-form. The normal as well as the aci-form may be electrolytically dissociated to a certain extent. Since, however, the pseudo- is always much weaker than the aci-form, the apparent constant (see Chap. IV., p. 130), in which undissociated pseudo- is included with undissociated aci-, will always be less than the real constant of the aci-form (see p. 129).

The apparent constants of the mono-nitro-phenols are of the same order.

Thus, Hantzsch and Salway, *Ber.*, 40, II., 1557 (1907), from conductivity results, find :—

K (para) = $0{\cdot}74 \times 10^{-7}$ K (ortho) = $0{\cdot}56 \times 10^{-7}$.

From the hydrolysis of Na salts at V = 32,

| | Per cent. hydrolysis. | K. |
|---|---|---|
| ortho- . . . . | 0·26 | $0{\cdot}5 \times 10^{-7}$ |
| para- . . . . | 0·23 | $0{\cdot}6 \times 10^{-7}$ |

According to Lowenberg, *Zeitsch. phys. Chem.*, 25, 385,

| | ortho. | para. | meta. |
|---|---|---|---|
| $K \times 10^{-7}$ | 0·83 | 0·12 | 0·089 |

It is probable that in the case of the ortho-compound the pseudo-form is a relatively strong, the aci-form relatively weak and the ratio aci/pseudo is high, as is shown by the yellow colour of the solid and aqueous solutions. The para-compound has probably a weaker pseudo-form, a stronger aci-form, and a low transformation ratio aci/pseudo. In all cases where the aci-form is not a very strong acid, the

colour will be due in a large measure to undissociated molecules, and therefore the dissociation constant derived from colorimetry will agree badly with that derived from conductivity. This effect is very evident in the case of ortho-nitro-phenol.

Hantzsch, *Ber.*, 39, I., 1103 (1906):—

| V. | Per cent. dissociated. | Per cent. coloured. |
|---|---|---|
| 64 | 0·25 | 0·44 |
| 128 | 0·36 | 0·46 |
| 256 | 0·51 | 0·77 |
| 1024 | 1·0 | 2·11 |

Some part of the total ion (second column) is no doubt derived from the pseudo-form. Leaving this out of account it will be seen that the amount of the coloured form dissociated is over 30 per cent. It should be noted, however, that these results are not confirmed by Scharwin, *Journ. Chem. Soc. Abstracts*, 98, II., 397, who finds that the dilution law holds for both colour and conductivity and that the two curves coincide. If the aci-form is much stronger so that practically all the coloured substance is present as ion, and the pseudo-form much weaker, then the colorimetric will agree with the electrometric dissociation constant, and conversely the agreement may be taken as a criterion of the strength of the aci-form.

Thus, Hantzsch, *loc. cit.*, p. 1103, gives the following table for di-nitro-phenol:—

| V. | Per cent. dissociated. | Per cent. coloured. |
|---|---|---|
| 512 | 18·3 | 19·9 |
| 1024 | 25·2 | 25·8 |
| 2048 | 32·6 | 31·9 |

In all cases a better agreement is to be expected in solutions which are moderately dilute, but not so dilute as to make the error on the colorimetric determination unduly large. Tri-nitro-phenol is a still stronger acid. The constant was obtained by Rothmund and Drucker, *Zeitsch. phys. Chem.*, 46, 827.

(1) By determining the concentration of the undissociated molecules by means of the distribution ratio (= 0·0281) between water and benzene. The constant was 0·164.

(2) By the conductivity method (at 25°).

The " constant " increased with increasing concentration, a behaviour which is characteristic of strong acids.

| | | |
|---|---|---|
| V | = 32 | 1024 |
| K | = 0·2 | 0·02 |
| 100 $\alpha$ | = 87 | 96 |

*Colour and Salt Formation of Organic Bases.*

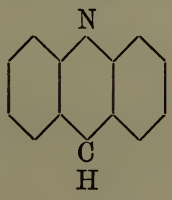
The evidence that organic bases can occur in two forms which are characterised by differences in colour and electrical properties is even clearer than in the case of nitro-compounds. Since amine bases can only form salts by the addition of acids without elimination of water, and can only manifest alkaline properties (*i.e.*, by ionisation into kathion and [OH′] after the addition of the elements of water, it is necessary to include another equilibrium, that of hydration, with those already stated for the nitro-compounds. The irregular effect of substitution upon the dissociation constant of, *e.g.*, the simple amines (see table, p. 18) may be attributed to the total resultant effect of the alkyl groups acting on both the hydration and the ionisation equilibria. Thus a base may seem to be moderately strong

when it has a high hydration and a low ionisation constant, and also *vice versâ*. A great increase of strength is, however, always observed when the hydrogen is completely replaced by alkyl, etc. Compounds such as tetralkyl ammonium hydroxide $NR_4OH$ will naturally show the true dissociation constant (corresponding to the high electro affinity of the kathion part) unmodified by the constant of hydration. The small amount of undissociated base cannot in such a compound be weighted by a large amount of neutral non-electrolyte amine, as, for example, $NH_4OH$ with $NH_3$. When therefore a compound of this class, *e.g.*, an alkyl acridonium hydroxide, appears to be much weaker than is to be expected from its structure, there is good reason to suppose that it has changed into a pseudo-form.

The analogy between the tautomerism of acids and that of bases is most simply shown by the acridine derivatives with only one strong basic position on the molecule, but similar changes of structure may be used to explain the amido phenyl-methanes with three such centres.

*Acridine Derivatives.*

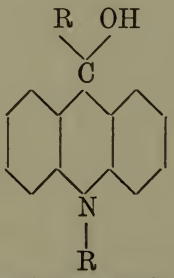
The investigation of these compounds was chiefly carried out by Hantzsch and his co-workers, *Ber.*, 22 and 23, 1899 and 1900, and Muller, *Ber.*, 43, 1910*.



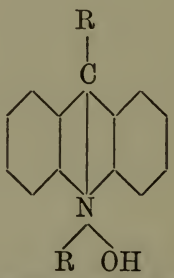

* A fuller account of the more numerous colour changes of the solid form under the influence of slight changes of solvents and other conditions, which are called chromo-isomeric changes fall outside the scope of this work.

Acridine itself has no visible colour, but gives with acids yellow salts which must be derived from an acridonium base.

The alkyl and aryl acridonium derivatives exhibit changes of colour and conductivity quite analogous to those of the nitro-compounds described above. These changes have been similarly explained by the transformation of a pseudo- into a baso-form, and *vice versâ*.




pseudo-form, acridol.

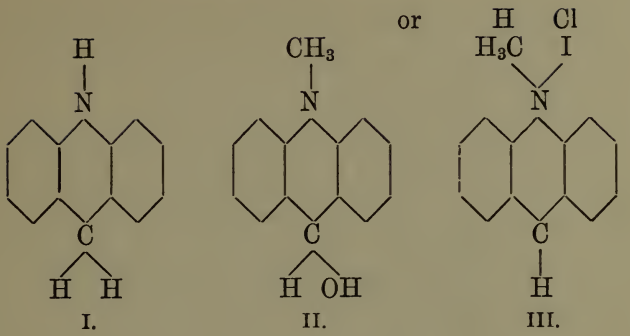



baso-form, acridonium.

The acridonium hydroxides as set free by strong bases from their salts are themselves strong bases. The conductivity of a solution of the base in water gradually falls, however, owing, it is supposed, to a spontaneous change into the acridol form which is so slightly dissociated that it may be considered a non-electrolyte.

The changes of constitution are confirmed by the evidence of the absorption spectra (Dobbie and Tinkler, *Journ. Chem. Soc.*, 87, 269 (1905); Tinkler, *Journ. Chem. Soc.*, 89, 856 (1908)).

Di-hydroacridine, which has necessarily the structure I., has an absorption spectrum closely resembling that of the compound set free by alkalies from acridine methiodide III. To this base is therefore assigned the carbinol structure II. Acridine methiodide itself resembles the hydrochloride in optical properties.

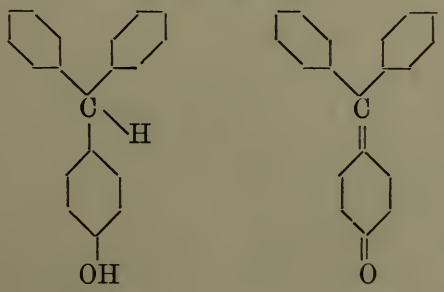



*Triphenyl-methane Compounds.*

The crystal violet group of dyes, including the rosanilines, brilliant green and methyl violet, are all capable according to their constitutions of undergoing the pseudo-baso change. There is evidence of unsaturation or free valencies in the compound di-triphenyl methyl from which they are derived $[C(C_6H_5)_3]_2$.

This easily unites with oxygen and halogens to form peroxides and halides as well as with other unsaturated compounds such as benzo-quinone. The compound itself is white, but gives yellow solutions in organic solvents.

The carbinol derivatives are colourless, but the p.-hydroxy carbinol on losing water gives orange fuchsone to which a quinone structure has been assigned.



The addition of one or more amino groups increases the colour; the salts of these compounds are true dyes, such as malachite green and magenta (see below).

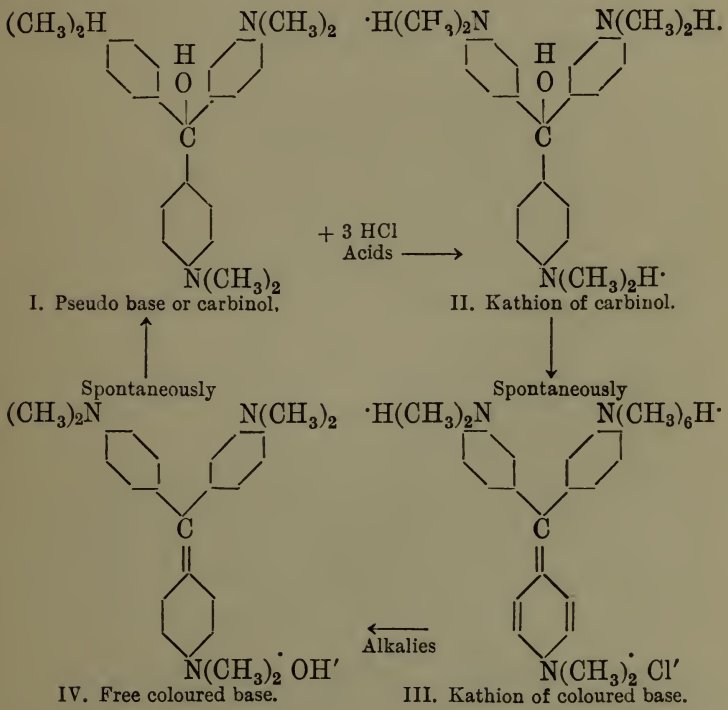
The base from which these compounds is derived is colourless in its most stable condition. The metastable coloured form of the free base can, however, often be prepared, *e.g.*, in the case of crystal violet, the hexa-methyl derivative of triamido triphenyl carbinol. If one equivalent of sodium hydroxide is added to a mol. of the crystal violet monochlorhydrate, the solution remains coloured and is strongly alkaline, but on standing the colour gradually fades and the conductivity decreases. Thus, before the change, all the base present, whether colour base or sodium hydroxide is highly dissociated, but after the change the alkali has combined with the hydrochloric acid and set free an equivalent of weak base. In some cases the fading may be quicker or even instantaneous.

The reverse change in the case of crystal violet may be carried out by carefully treating the colourless bases with acids in the absence of water. Colourless salts are produced which dissolve in water to form colourless solutions. When there are three equivalents of acid present to one of base, the salt is strongly hydrolysed. On standing, the solution gradually becomes coloured, while the conductivity and therefore the degree of hydrolysis is further increased.

The salt prepared by adding one equivalent of an acid to the coloured or true base is scarcely hydrolysed at all. Thus while the first basic centre of the coloured base is strong, the second and third are even weaker than the corresponding centres of the colourless base.

It is considered that the pseudo-base is a carbinol, the OH being attached directly to the central carbon atom. Hydrochloric acid may be added to each of the dimethylamino groups, the kathion II. is formed, and since

all the centres are weak, hydrolysis occurs. Water is then eliminated with the formation of the ion of the true base III., of which the centres (2) and (3) are highly hydrolysed, but (1) is strong. Addition of alkali then produces the strong base IV.*




The behaviour of these compounds as indicators may be represented well by these formulæ. The long range of constant blue or violet colour in neutral or alkaline solutions corresponds to the formation of a salt of the strong base, or in the more alkaline solutions to the metastable

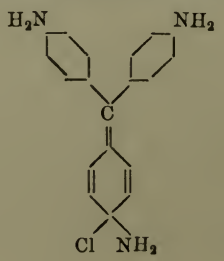
* According to F. Baker, *J. Chem. Soc.* 91, 1490 (1907), the absorption spectra show that the salts are derived from a carbonium rather than an

colour base. The fading in the more alkaline solutions is due to the slow formation of the carbinol. The colour changes in acid solutions are due to the diminution of hydrolysis, and the more complete salt formation on centres (2) and (3). The fading and recovery of colour have been shown by Adams and Rosenstein, *Journ. Amer. Chem. Soc.*, 36, 1452 (1914), to be reversible reactions, and therefore a true molecular change appears to take place rather than the formation of colloidal complexes. A spectrophotometric examination is said to show that three coloured substances—a violet, green and yellow—are necessary and sufficient for all the colours observed in the more acid solutions of crystal violet, and these colours are assigned to the monodi- and trihydrochloride and their ions which are progressively formed in increasingly acid solutions.

| $C_{25}H_{30}N_3Cl$ | $C_{25}H_{30}N_3Cl(HCl)$ | $C_{25}H_{30}N_3Cl(2HCl)$ |
|---|---|---|
| violet | green | yellow |

To sum up, the difference between a coloured and colourless base is by the preceding arguments attributed to the migration of the OH from the strongly basic position to the central carbon atom, with simultaneous change of quinoid to benzoid disposition of valencies. The quinoid base owes its strength to the cause stated on p. 107, *i.e.*, the

ammonium base. Thus, the monochloride of a triamido compound would be represented by the formula (see also Baeyer, *Ber.*, 38, 569, 1156 (1905))—



impossibility of dehydration with formation of a neutral non-electrolyte compound.

*The Phthalein Indicators.*

The condensation products of phthalic anhydride and phenols, of which phenolphthalein is the simplest representative, are like the last class derivatives of triphenyl (or tri-aryl) methane, carbinol, and therefore similar explanations may be proposed for the colour changes consequent on the formation of salts. A benzoid and a quinoid structure may be assigned to the colourless free pseudo-acid and the coloured salt-forming acid respectively. The evidence for a change of structure is similar to that already given, namely, the isolation of coloured and colourless organic derivatives corresponding to the salts and free compound respectively.

The compounds present in aqueous solutions are probably represented by the formulæ on p. 114.

The colourless compound in acid solution is the lactone I. On the addition of alkalies the red salt of the quinoid molecule 2 is formed either directly with the formation of one molecule of water, or indirectly by the addition of one molecule of water, giving the carbinol III., with the subsequent loss of two molecules of water.

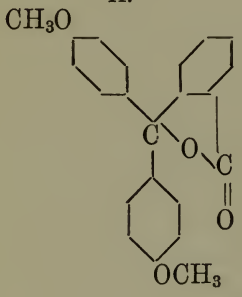
A further addition of alkali gives the carbinol III. with salt formation on the phenolic hydroxyls (Acree and Slagle, *Amer. Chem. J.*, 42, 115 (1909); Green and Perkin, *Proc. Chem. Soc.*, 20, 50 (1904); Meyer and Spengler, *Ber.*, 38, 1322 (1905)).

Many derivatives of phenolphthalein:—Ethers, esters, oximes, anilides, salts (with acids), and double salts (with metal chlorides) are now known, and these may be either colourless or red. The methyl ester is red, and since it can also be saponified, giving the red alkali salts, an identity of

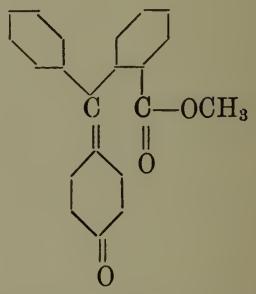
structure is highly probable (I.) (Green and King, *Ber.*, 40, 3724 (1907) ).

The di-methyl ether (II.) which cannot by its constitution be quinoid is colourless and is most likely derived from the lactone (Haller and Guyot, *C. R.*, 120, 296 (1895)).

II.

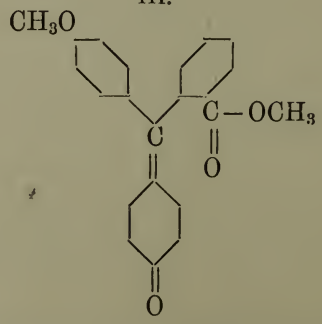



I.




The isomeric monomethyl ester is orange (Green and King, *loc. cit.*) (III.). Both these compounds are insoluble in alkalies.

III.

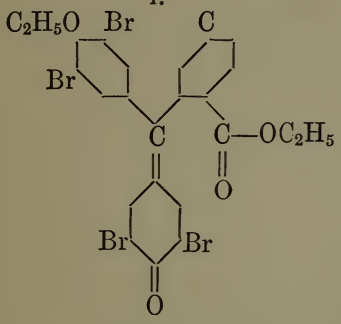



The bromo derivatives of phenolphthalein undergo similar changes.

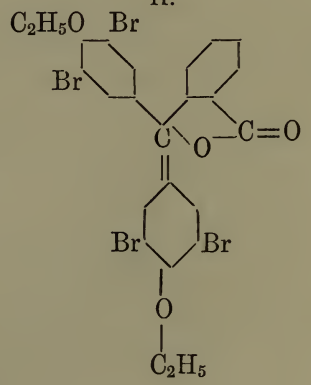
Thus the tetra-bromo compound (prepared by brominating phenolphthalein) was dissolved in less than the calculated amount of sodium hydroxide, filtered, to the filtrate $AgNO_3$

was added. The blue silver salt $C_{20}H_8O_4Br_4Ag_2$ was dried, suspended in dry benzene, and ethyl iodide was added. The liquid turned yellow owing to the formation of the ether ester I., which could be obtained in yellow crystals melting at 160°—163°. When kept for long periods, melted or recrystallised from alcohol it is converted into the lactoid ether II. The quinoid ether ester I. when saponified yields a colourless compound, probably the lactoid monoethyl ether III. (Meyer and Marx, *Ber.*, 40, 1437 (1907)).

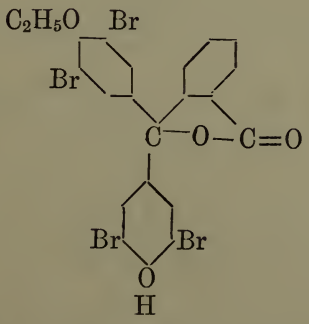
I.




II.

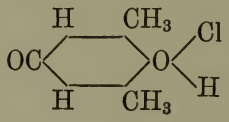



III.

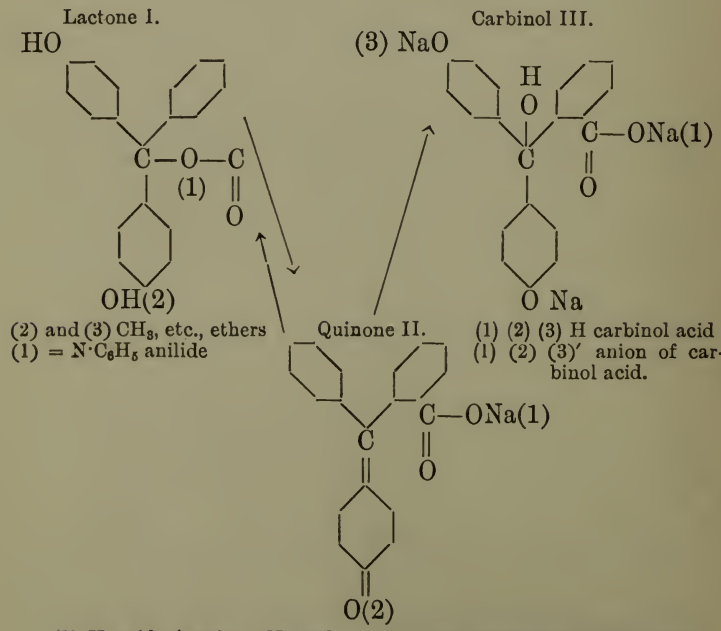



The acid salts and double salts of phenolphthalein have been chiefly investigated by Meyer and Hantzsch, *Ber.*, 40,

3479 (1907); Hofmann and Kirmreutther, *Ber.*, 42, 4856 (1909). They are red, and have therefore probably the quinone formula, and should be represented as oxonium salts similar to the hydrochloride of dimethylpyrone (Collie and Tickle, *Journ. Chem. Soc.*, 75, 710 (1899) ).

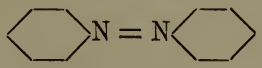


In the diagrammatic representation of all these changes the centres of substitution, the carbonyl and the two phenolic positions are numbered (1), (2) and (3).



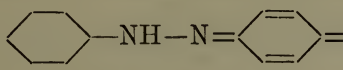
*Amino-azo-compounds.*

The basis of the colour in these compounds is according to the simple theory, the chromophore group:



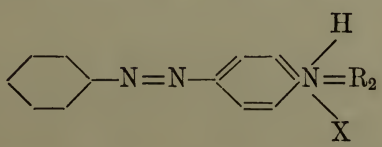
The substitution of hydrogen by amino groups, etc., produces colour bases, and a further substitution by acid groups (sulphonic, etc.) produces an amphoteric molecule with still greater possibilities of tautomeric change and ionisation equilibrium. Azo-benzene may be considered as the parent substance, and this has the azoid formula given above. The solid is orange yellow, and it gives yellow solutions in organic solvents. The derivatives are also generally yellow in organic solvents or as alkali salts, but red in acid solution and red or violet as solids. The simplest hypothesis which would account for this was to assign to the yellow series an azoid, and to the red a quinoid formula. The two series of alkyl-amino-azo benzene would be represented by—

*Quinoid salt* (or hydrated base), colour red or violet:



Favoured by the solid state and neutral organic solvents.

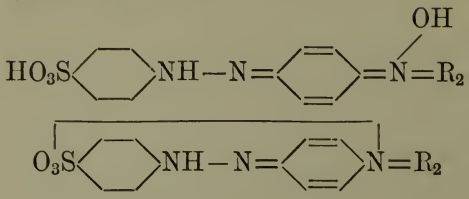
*Azoid salts* (or hydrated bases), colour, orange or yellow.



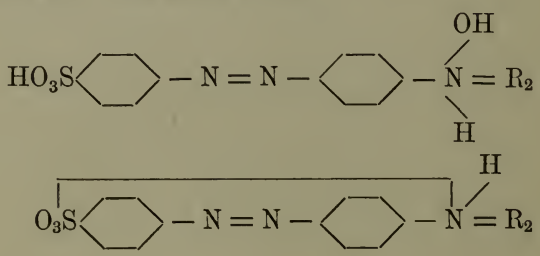
Favoured by solution in water, alcohol and acetone. The coloured salts of both types can, under suitable conditions, be isolated (Hantzsch and Hilscher, *Ber.* 41, 1171 (1908)).

A similar tautomerism can be stated for those diazo compounds in which the substitution by an acid group produces an amphoteric molecule.

The red quinoid forms :—



(*Free amphoteric molecule*) or (*inner salt*) are changed partly on solution in water, completely on the addition of alkali into the salts of the azoid forms—



The possibility of this tautomerism is, therefore, present when an unsaturated group $NH_2$, OH, etc., is present with an azo group. The position of the $NH_2$, etc., groups which is in most cases ortho- or para- to the azo, affects somewhat the tendency to pass into the quinoid form. Thus hydrochloride of meta-diamido azo benzene is orange in the solid state, while that of the para compound crystallises in dark steel blue needles, and resembles generally the quinoid forms of these compounds. The mere substitution of alkyl, etc., which does not affect the general structure only alters the position of the head of the absorption band without affecting the general character of the spectrum.

These points will now be illustrated by a few examples from other diazo compounds. In a paper by Hewitt, *J. Chem. Soc.*, 105 and 106, 2193 (1914), which contains a useful summary of previous results it was shown that where such tautomeric change is excluded by the structure, the colour change is also absent or small in amount. The tautomeric change occurs in compounds in which the $NO_2$, CO or OH groups between which interaction takes place are on different nuclei. Thus the head of the absorption band of para-acetyl benzene azophenol in alcohol—

$$CH_3CO - C_6H_4 - N = N - C_6H_4(OH)$$

lies at 2750 (brown), while on adding alkali it changes to 2100 (purple)—

$$CH_3 - C(OK) = C_6H_4 = N - N = C_6H_4 = O.$$

In the case of the phenyl hydrazone—

$$CH_3 - C(=N - NH - C_6H_5) - C_6H_4 - N = N - C_6H_4 \cdot OH$$

the addition of alkali, which only results in the substitution of OK for phenolic OH only moves the band from 2450 to 2300. When, on the other hand, the $NO_2$ and OH, etc., between which the interaction takes place are on the same benzene nucleus, no quinoid form is produced, and the change in light absorption is much slighter. The salts of such compounds would have the formulæ—

$$\overset{4}{NO_2} - C_6H_4 - N = N - C_6H_3(-\overset{3}{NO} - OK) = \overset{4}{O}$$

$$\overset{4}{NO_2} - C_6H_4 - N = N - C_6H_3(-\overset{3}{CH} - OK) = \overset{4}{O}.$$

Thus the alcoholic and alkaline solutions of the latter compound (para-nitro benzene azo salicyl aldehyde) are both yellow.

The phenyl hydrazone while yellow in neutral organic

solvents is purple in alkalies, and the redistribution of valencies must in these cases produce a quinoid form.

$$NO_2 - C_6H_4 - N = N - C_6H_3(CH = N - NHC_6H_5) - OH$$
$$KO - ON = C_6H_4 = N - N = C_6H_3(= CH = N - NH - C_6H_5) = O.$$

When the tautomeric change takes place, as usually with indicators of this class between the azo and the substituting group, it appears to occur somewhat more easily when the latter is in the ortho than when it is in the para position (Tuck, *J. Chem. Soc.*, 91, I., 450 (1907)).

The absorption spectra of para compounds of the type $R - C_6H_4 - N = N - C_6H_3(- R) - OH$ in which R is an alkyl radicle, as well as those of their ethers and benzoyl derivatives are similar to those of azo benzene. The ethers of the compounds in which the OH is ortho to the nitrogen were also found to be azoid, but the ortho compounds themselves had a different spectrum.

The structures might be represented:—

$$CH_3 - C_6H_4 - N = N - C_6H_3(\overset{2}{C}H_3)\overset{4}{O}H \text{ para (benzoid)}$$

and

$$CH_3 - C_6H_4 - NH - N = C_6H_3(-\overset{3}{C}H_3) = \overset{2}{O} \text{ ortho (quinoid).}$$

It must be noted, however, that the benzoyl derivatives of the ortho compound also have the quinoid spectrum.

Both ortho and para diazo indicators pass into the quinoid form with great ease in the presence of acids.

*Substitution without Change of Structure.*

Provided that the possibility of tautomeric change is unaltered, a mere substitution of alkyl groups, etc., in the nuclei or side-chains does not profoundly affect the optical properties. The position of the heads of the absorption bands may, however, be slightly altered (see Hartley,

*J. Chem. Soc.*, 51, 152 (1887); Baly and Tuck, *ibid.*, 89, 985 (1906); Hantzsch, *Ber.*, 42, 2132 (1909); Hewitt and Thole, *J. Chem. Soc.*, 97, 511 (1910)).

The heads of the most persistent bands of greatest wave length are found at the following frequencies $\left(\frac{1}{\Lambda}\right)$ :—

P. amino azo benzene, 2,000.

P. dimethyl amino azo benzene, 1,900.

P. amino benzene azo phenol, 1,800.

P. dimethyl amino benzene azo phenol, 1,800.

The addition of HCl in all cases moves the absorption further towards the red.

It is impossible to make more than a small selection from the literature on this subject. The typical change of colour, the similarity of the absorption spectra and the possibility of the quinoid form are all common to a great variety of compounds. The four typical absorption bands of azo benzene or the amino azo benzenes have their heads at $1/\Lambda = 1{,}900$, 2,300, 2,600, 3,200, according to Baly and Hampson, *J. Chem. Soc.*, 107, 248 (1915). Like conditions produce the same colour and absorption spectrum, whether the compound is purely basic like dimethyl amino azo benzene or amphoteric with a predominating acid character like helianthin. In the yellow alkaline solutions the former must be present as undissociated base or neutral basic anhydride, the latter as anion.

The spectra, though similar, are not identical; the main absorption band of methyl orange being nearer to the red (Hantzsch, *Ber.*, 46, 11, 1537 (1913)).

Even this slight difference may be explained as due to the auxochromic effect of the $HSO_3$ and not to its acid character. That the damping effect of the increased molecular weight may be a sufficient explanation is shown by the fact that the introduction of a neutral group $COOC_2H_5$ also

produces a compound $(CH_3)_2N \cdot C_6H_4 \cdot N_2 \cdot C_6H_5COOC_2H_5$ with an absorption spectrum almost identical with that of methyl orange. It is evident that the polarity of the substituting groups may vary widely while leaving unaltered the general structure of the molecule and the nature of the colour changes. Yet it is, of course, all important in determining the behaviour of the substance as indicator, *i.e.*, the $[H^{\cdot}]$ at which the colour change occurs. As will be seen in the next chapter (p. 130) a good indicator for titration purposes must not have too high an acid or basic dissociation constant.

*Amino Azo Benzene and Alkyl Derivatives.*

In accordance with the pronounced basic character of amino azo benzene it gives a well defined series of salts with acids. The oxalate is prepared by dissolving the base in excess of ethereal oxalic acid. Curiously this compound unlike the hydrochloride is yellow. It possesses an absorption spectrum similar to that of the sodium salt of methyl orange, or pure methyl orange itself in alcoholic solution, but not similar to that of azo benzene. The halogen alkylates on the other hand produced by the addition of RX to alkyl amino azo benzenes do possess the azo benzene spectrum. These compounds, therefore, must possess the azoid formula—$C_6H_5 - N = N - C_6H_4 - NR_2 = RX$, while all the other compounds whether yellow or red must have another structure. But the quinoid formula is already appropriated for the red compounds. It was considered by Hantzsch that the optical difference between the yellow and the red solutions, which consisted in a shift of the principal absorption bands, is best expressed by a valency and not a position isomerism. The ordinary yellow and red solutions are considered to

contain valency isomers of the quinoid variety. Corresponding to the solutions there are solid forms. These are in the case of amino azo benzene :—

(1) The ordinary stable form of the pure compound, violet-red corresponding to the solid alkyl substituted forms, solid helianthin, etc.

(2) A flesh-coloured form which is precipitated from the ethereal solution by HCl or $CH_3COCl$ (Thiele, *Ber.*, 36, 3695 (1903)). This does not appear crystalline even under a high power. It probably belongs to the yellow (quinoid) series coloured by a trace of the red. A flesh-coloured solution of dimethyl amino azo benzene may also be obtained by careful acidification of the yellow aqueous solution.

(3) An almost black form (hydrochloride) which has no analogue in the dialkyl substituted series. To this is given the formula $C_6H_5 - NH(HCl) - N = C_6H_4 = NH$.

It is yellowish brown by transmitted light and crystallises in a different system from (1). Excluding this form but including the benzoid (azoid) there are three main types which can be recognised throughout the diazo indicators.

(1) Yellow benzoid : Azo benzene. Halogen alkylates (see p. 122).

(2) Yellow quinoid : Amino azo benzene chloride (solid). The yellow acid salts. Solutions of alkyl amino azo benzenes and their substitution products in pure alcohol and alcohol with sodium ethylate. The sodium salts of the same compounds in water.

(3) Red quinoid. The compounds and their substitution products in the pure state and in solutions of moderately high acidity.

This classification originated from an examination of the curves of absorption. The resemblance of (2) to (3) is

much closer than that of either to (1), and this although (1) and (2) are yellow while (3) is red.

Intermediate colours, whether in solution or in the solid state, may be regarded as due to mixtures of the pure forms, since sometimes by special precautions the intermediate tint can be made to disappear, or again the separate constituents of a solid may be detected by the microscope. Thus the free acid, helianthin, is orange as usually prepared. This colour appears to be due to a trace of salt, produced by combination with the ammonia of the air or the soda or lime of the glass. Pure helianthin has been prepared (Hantzsch) by adding ligroin to the pyridine solution. A solvate is precipitated which loses its pyridine at 100°.

The conditions of the existence of forms 2 and 3 above could be verified with this preparation. The purest alcohol prepared by distillation from lime, then from metaphosphoric acid dissolves pure red helianthin, giving a pure yellow solution. This solvent favours the yellow form to such an extent that the addition of glacial acetic acid does not change the colour until a considerable excess of acid is present (Waddell, *Chem. News*, 77, 131 (1898) ).

If, however, dry hydrochloric acid gas is passed into the alcoholic solution it becomes red. The hydrion concentration of acetic acid in alcohol is low, that of hydrochloric acid is higher. The red colour appears to be chiefly a function of [H·] (see p. 145, Chap. IV.).

The yellow colour in alcohol is not altered on the addition of sodium ethylate, and is practically identical with that of the sodium salt in water. Even the free methyl orange in water consists mainly of the yellow form (80—90 per cent.) (Hantzsch). Evidently colour and ionisation by no means run on parallel lines here.

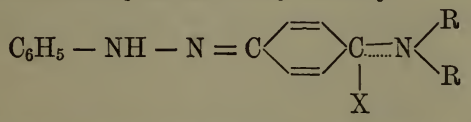
The formulæ which have been assigned to the valency isomers will now be briefly given. From their nature it is

almost impossible either to prove or to disprove them in the present state of knowledge, but they usefully supplement the tautomeric theory already given.

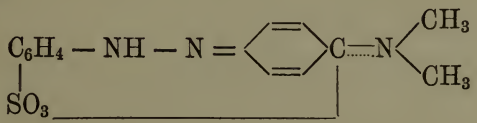
The valency isomers of the diazo compounds have been represented by Hantzsch, *Ber.* 46, ii., 1537 (1913), on the Werner plan, according to which nitrogen has three principal valencies (full lines) and one auxiliary valency (dotted lines). A simple example of valency isomerism is methyl-pyridonium iodide.

Colourless. Yellow.

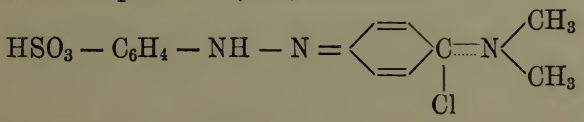
So in the most strongly coloured (red) amino azo compounds the amino nitrogen is supposed to be united to the benzene nucleus by an auxiliary valency.



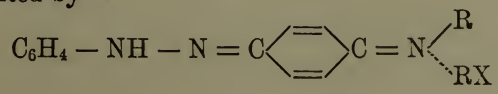

The red inner salt of methyl orange may similarly be written—



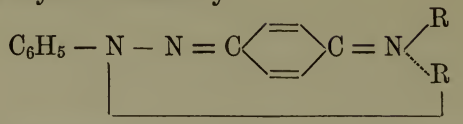

and the compound in (HCl) solution



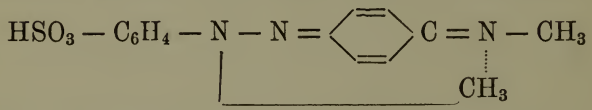

The yellow salts of dialkyl amino azo benzenes would be represented by—



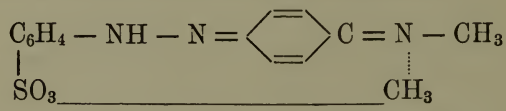
The free anhydrous bases by—



The yellow solution of methyl orange in alcohol by—



The yellow inner salt of methyl orange by—



The tautomeric changes which have been given as the cause of that change in the colour of amino azo benzenes which depends upon change of [H·] may be summarised as follows:—

(1) Benzoid-quinoid. A hydrogen atom is attached to a diazo nitrogen, the amino benzene nucleus becomes quinoid and the amino nitrogen is connected with it by a double bond.

(2) Subsidiary valency. In the yellow forms the amino nitrogen is united by an auxiliary valency to one of the alkyl groups. The free valency of this is either united to the free valency of one diazo nitrogen (free anhydrous bases) or to the acidic radicle on the other benzene nucleus (inner salts), or combined with X H (diazo N with H) respectively to form the yellow acid salts (of basic amino azo benzenes).

In the red forms the auxiliary valency of the amino nitrogen is transferred to the carbon, and it is the carbon which now forms a valency ring with the diazo nitrogen or acidic group, or adds on X to form hydrochlorides, etc.

# CHAPTER IV

## MEANING OF THE IONISATION CONSTANT OF INDICATORS

The combination of the tautomeric and ionisation equilibria. Electrical and optical constants. The ionic equilibria of the phthalein and amido azo indicators. The determination of indicator constants. Tables of constants. The classification of indicators. The relation of indicator exponents to colour changes. Effect of temperature upon indicator exponents. The use of indicator constants in choosing indicators for various purposes. The sensitivity of the eye to change of colour intensity. The change of intensity in different parts of the transition interval. The best indicator concentration. The titration exponent or best tint for the end point. Comparison between one and two colour indicators. The effect of alcohol upon indicators and hydrolysis generally.

The conception that indicators are acids and bases which take part freely in the electrolytic equilibria has obviously the advantage that all the equations of these equilibria could be directly applied to the transformations of indicators. It will be shown that this advantage need not be foregone on account of the probability that the colour changes are directly dependent upon those structural changes which are called "tautomeric." For whatever else indicators may be, they are certainly also acids or bases or amphoteric compounds, that is to say, the change of colour is always a function of $[H^{\cdot}]$.

If the colour change is not at all, or only slightly influenced by $[H^{\cdot}]$, or is easily brought about by slight changes of solvent temperature illumination, etc. (polychromic compounds), then the compound is *ipso facto* useless as an indicator. An indicator, however, like paranitro-phenol, which is sensitive chiefly to changes of $[H^{\cdot}]$

and which forms well-defined salts, is no more to be denied a participation in the ionic equilibria than a compound like phenol or benzoic acid. The subject of this chapter is a consideration of how the tautomeric should be related to the ionisation equilibria, and whether constants for the latter can be formulated which shall include the former. It will be shown that this can be done, provided that the compound fulfils the following requirements of a good indicator—

(1) The hydrogen or hydroxyl ions must participate in the colour changes, so that the colour is a function of [H·].

(2) The tautomeric change must be almost instantaneous. Thus the utility of cyanin and haematein is impaired by the slowness of their colour change.

(3) The colour change must be due to the tautomeric change only, and must be brought about only by the change in [H·] and [OH′], and not by that of any other molecules or ions in solutions. Other requirements, which do not concern the immediate subject of this chapter, will be noted in their place (Salm, *Zeitsch. Elecktrochem.*, 10, 344 (1904) ).

It is assumed that the tautomeric changes can be quantitatively expressed by the laws of chemical equilibrium. This assumption seems reasonable, in view of the observation that both the colour changes and the ionisation changes obey these laws, although the constants for the two kinds of change may differ in the case of the same indicator. Since the ions are in equilibrium with H· and OH′ and the other molecules (tautomers, etc.) are in equilibrium with the ions, the colour change must be a function of [H·] and [OH′], and therefore the above condition with respect to the tautomeric changes is sufficient for the fulfilment of requirement (1), above.

A numerical example due to Thiel will make this clear. Suppose that the concentrations of dissociated and undissociated para-nitro-phenol are not equal to those of the colourless and coloured form respectively, but that 1 per cent. of the free acid and 80 per cent. of the ion exist as the yellow tautomer. In a 0·0001 N. solution of the indicator ($K = 7 \times 10^{-8}$) 3 per cent. is dissociated, therefore there is present $0{\cdot}97 + 2{\cdot}4 = 3{\cdot}4$ per cent. of the yellow form. In a solution 0·001 N. with respect to $H^{\cdot}$ the dissociation is only 0·007 per cent., and the yellow tautomer is 1·006 per cent. of the whole. In a faintly alkaline solution of which $[H^{\cdot}] = 1 \times 10^{-8}$ the indicator is dissociated to 99·97 per cent. and the percentage of yellow form is 79·9. Thus there is a constant for the colour change which is not identical with that of ionisation.

The relations between the two constants have been worked out by v. Zawidski, *Ber.*, 36, 3325 (1903); 37, 153 (1904); and by Noyes, *J. Amer. Chem. Soc.*, 32, 815 (1910).

The two tautomeric forms of the molecule M will be represented by $HM_1$, $M'_1$ (or $M_1OH$,$M^{\cdot}_1$) and $HM_2$, $M'_2$ (or $M_2OH$, $M^{\cdot}_2$).

It is to be supposed that in acid solution the indicator acid is present mainly as $HM_1$ and its ions (one colour); in alkaline solution as the ion $M_2$ and the acid $HM_2$ (other colour).

These relations are expressed by the usual equations.

$$[H^{\cdot}] \times [M_1'] = K_1[HM_1] \quad . \quad . \quad (1)$$
$$[H^{\cdot}] \times [M'_2] = K_2[HM_2] \quad . \quad . \quad (2)$$

To which must be added that of tautomeric change :—

$$HM_1 \rightleftarrows HM_2$$
$$[HM_2] = K_T[HM_1] \quad . \quad . \quad . \quad (3)$$

The tautomeric change may be calculated as if it took place either between the molecules $HM_1$ and $HM_2$ or between the ions $M_1$ and $M_2$, or between both molecules and ions; because the tautomeric constant of the ions is not independent of that of the molecules, but is connected with it by the equation—

$$M'_2 = M'_1 \frac{K_2 K_T}{K_1}.$$

In acid solution nearly all the indicator is in the $M_1$ form, and since it is not in any case a strong acid it will be present almost exclusively as $HM_1$. Therefore, the constant $K_T$ from equation (3) must be small.

In alkaline solution the indicator is almost all in the $M_2$ form, and most of this is the ion $M_2$. Therefore, the constant

$$\frac{M'_2}{M'_1} = \frac{K_2 K_T}{K_1} \text{ must be large.}$$

It has already been stated, however, that $K_T$ is small. Therefore $K_2$ must be much larger than $K_1$. This is the formal expression of the fact that indicator acids (and bases) when set free by strong acids and bases appear first in an aci-form $HM_2$, with a relatively high dissociation constant, and then change spontaneously into a pseudo-acid $HM_1$ with a very low dissociation constant.

The apparent dissociation constant of the indicator as found by electrical conductivity will not be identical with that of either acid, but will contain the sums of the two kinds of ions and molecules.

$$K_A = \frac{[H^\cdot]\,[M'_1 + M'_2]}{[HM_1 + HM_2]} \quad . \quad . \quad . \quad (1)$$

$$K_B = \frac{[OH']\,[M^\cdot_1 + M^\cdot_2]}{[M_1OH + M_2OH]} \quad . \quad . \quad . \quad (2)$$

The constants $K_A$ and $K_B$ may be obtained in terms of $K_1$ and $K_2$, p. 129, by multiplying

(1) by $HM_1 = HM_2/K_T$

(2) by $M_1OH = M_2OH/K_T$

Then
$$K_A = \frac{K_1 + K_1K_T}{1 + K_T}$$
$$K_B = \frac{K_1 + K_2K_T}{1 + K_T}$$

As already stated, practical indicators are such as turn almost completely into the $M_1$ form in high $H^{\cdot}$ or $OH'$ concentrations and into the $M_2$ form in low $H^{\cdot}$ or $OH'$ concentrations. There are three principal cases (Noyes, *loc. cit.*):—

(*a*) The indicator is colourless in acid and coloured in alkaline solution. Hence $HM_1$, $BM_1$ and $M'_1$ are colourless; $HM_2$, $BM_2$ and $M'_2$ are coloured. The constant $HM_2/HM_1$ must be small.

(*b*) The indicator is coloured in acid and colourless in alkaline solution. Hence $HM_1$, $BM_1$ and $M'_1$ are coloured; $HM_2$, $BM_2$ and $M'_2$ are colourless, and $M'_1/M'_2$ must be small.

(*c*) The indicator has different colours in acid and alkaline solutions. Hence $HM_1$, $BM_1$ and $M'_1$ have one colour, $HM_2$, $BM_2$ and $M'_2$ have another colour, and both $HM_2/HM_1$ and $M'_1/M'_2$ must be small.

The last case must be the normal one for tautomeric compounds if ultraviolet as well as visible colour is taken into consideration, and if it is strictly true that every change of constitution is accompanied by change of colour.

In determining the electrometric constants, ions or molecules present in very low concentration may be omitted from equations (1) and (2), p. 130, and in determining colorimetric constants, ions or molecules which are either present in very low concentration or colourless may be omitted.

The electrometric constants will be in the three cases :—

$$(a) \qquad \frac{[H\cdot]\,[M'_1 + M'_2]}{[HM_1]} = K_1 + K_1K_T$$

$$= K_1 \text{ (since } K_T \text{ is small)}$$

$$(b) \qquad \frac{[H\cdot]\,[M'_2]}{[HM_1 + HM_2]} = K_2 + \frac{K_2K_T}{K_T + 1}$$

$$= K_2$$

$$(c) \qquad \frac{[H\cdot]\,[M'_2]}{[HM_1]} = K_2K_T$$

The colorimetric constant will in all cases have the value—

$$\frac{[H\cdot]\,[M'_2]}{[HM_1]} = K_2K_T$$

Since in case (*a*) $M'_1$ is colourless and in case (*b*) $HM_2$ is colourless.

In case (*c*) the colorimetric is identical with the electrometric constant.

When, as in the present subject, changes of colour are of more importance than those of electrical properties the colorimetric constants $K_2K_T$ may be written simply $K_A$ or $K_B$.

These apparent dissociation constants will be found colorimetrically from the relative concentrations M′, M· of the coloured salt tautomer or HM, MOH of the coloured acid or base tautomer.

$$\frac{[H\cdot] \times [M']}{[HM]} = K_A \quad . \quad . \quad . \quad (1a)$$

$$\frac{[OH'] \times [M\cdot]}{MOH} = K_B \quad . \quad . \quad . \quad (1b)$$

If now $x$ and $1-x$ are the fractions of the indicator acid transformed and not transformed into salt after the addition of some alkali, then

$$\frac{1-x}{x} = \frac{HM}{M' + BM}$$

The total salt M′ + BM is, however, equal to $M'/a_s$ where $a_s$ is the degree of ionisation of the salt. Hence

$$\frac{1-x}{x} = \frac{[HM]}{[M']/a_S}$$

And from equation (1*a*)

$$[H\cdot] = \frac{1-x}{xa_S} \cdot K_A \quad . \quad . \quad . \quad (2a)$$

So in the case of a basic indicator if $x$ is the amount transformed into free base by the addition of alkali—

$$\frac{1-x}{x} = \frac{[M\cdot]/a_S}{[MOH]}$$

And from equation (1*b*)

$$[OH'] = \frac{x\,K_B}{(1-x)\,a_S} \quad . \quad . \quad . \quad (2b)$$

or

$$[H\cdot] = \frac{(1-x)\,a_S\,K_W}{x \qquad K_B}. \quad . \quad . \quad (2b)$$

If the indicator is considered as an acid in all cases, then the constant $\frac{K_A}{a_S}$ found will be equal to $\frac{a_S K_W}{K_B}$.

These equations give the amount of colour change as a function of [H·] and of the apparent constants. They define the relative change of colour for any change of [H·], within as well as beyond the range of visibility.

The degrees of dissociation $a_S$ may be considered to be constantly equal to unity, at low and moderate concentrations.

It might be concluded then that for all practical purposes the apparent constants can completely replace the real constants (of each tautomer). This conclusion is quite correct in theory if restricted to the usual cases of neutralisation and hydrolysis.

For the transformed part of the ion is supposed to bear a constant ratio to the total ion, and likewise the transformed part of the molecule a constant ratio to the total molecule, as in the example on p. 129.

The ratio of the transformed part of the electron compound to the untransformed part of the hydrogen compound as a function of [H·] is the indicator constant. It must also express the hydrolysis of the pure indicator salt as found colorimetrically, because hydrolysis is simply a special case of colour change with change of [H·] when the latter is derived from pure water.

It is necessary, however, to distinguish carefully between change in total amount of salt, etc., by change of [H·] (which also brings about change of constitution), and change of ionisation by the addition of a common or other ion, *i.e.*, excess of indicator salt or neutral salt. It is probable that the latter change is not accompanied by change of colour, the indicator salt, whether present as electron compound (ion) or as metal compound (salt), having the same colour as in the case of the inorganic salts mentioned in Chap. II., pp. 72, 73 (or in that of the salts of phenolphthalein or para-nitro-phenol, whether present in solution or as solids) (see also Chap. III.).

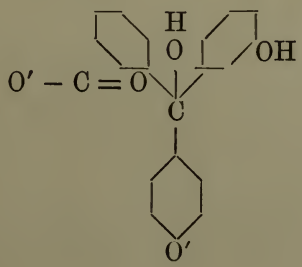
The assumption that all the $M_1$ salt, whether ionised or not, has the same colour is evidently implied in the equations (2*a*) and (2*b*), p. 133, which take account of the incomplete salt dissociation.

### *The Relations between the Electrolytic and Tautomeric Equilibria of some Indicators.*

*Phenolphthalein Group.*—It has been already shown how the colour changes of phenolphthalein which are apparently simple and can be expressed by one or two constants (see

pp. 143) in reality depend upon a series of ionic, tautomeric, and hydration equilibria (Chap. III.). The intermediate forms are known since they have been stabilised as ethers, esters, etc. The hydrogen compounds exist in aqueous solution in a state of incomplete equilibrium, therefore any or all of them may be present simultaneously. Thus the lactone requires a certain equilibrium concentration of quinoid molecule (formed by intra-molecular rearrangement) and of carbinol (formed by hydration).

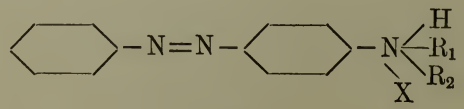
The pure compound as solid or in neutral solution is present wholly or chiefly as lactone. The lactone must be regarded as the pseudo-acid of phenolphthalein, and has a benzoid structure. The addition of alkali opens up the lactone ring, producing a true acid with change of structure to the quinoid. This is red, whether as ion or as sodium salt in solution or the solid state. Together with this there will possibly be present some, if only a small amount, of the ion of the lactone which will act as a very weak acid in virtue of its phenolic hydroxyls. Also even in moderately alkaline solution the sodium salt of the other true acid, the colourless carbinol, has begun to appear (Acree and Slagle, *loc. cit.* on p. 113, Chap. III.). An increased alkali concentration changes the compound more completely into the colourless carbinol form (salt or ion), and salt formation may take place also on the other hydroxyls.



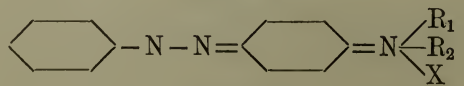
It is evident that the dehydrating effect of alcohol, etc., may have various unexpected results on these complicated equilibria (see p. 177).

*The Amino-Azo Group.*—Since the amino-azo benzene compounds all show much the same changes of colour as the [H·] of the solution containing them is changed, and the apparent ionisation constant can be equally well written as that of an acid $K_A$ or that of a base $K_B = K_W/K_A$, it is clear that for purposes of calculation it is not a matter of the first importance to know whether the compound is to be considered as an acid or as a base. But the distinction has a certain theoretical interest as leading to a decision, whether the effects of the addition of neutral salts, organic solvents, etc., are in accordance with those predicted by the ionic theory. It is interesting to know also whether the conditions under which indicators pass into the colloidal state or form well defined salts either with acids or bases can be predicted from the known positive or negative electro affinities of certain parts of the molecule. In Chap. III. it was shown that the alkyl amino-azo benzenes could be represented by two tautomeric forms each of which may be present as a free base, a salt or a kathion.

The quinoid and azoid formulæ proposed are :—



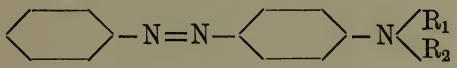
*Azoid.*



*Quinoid.*

In the kathion, [·], and in the base, OH, takes the place of X. The quinoid is by its constitution the stronger base,

since it cannot pass into a neutral compound with loss of water. On the other hand the base present in the yellow alkaline solution may appear weak merely because it is largely transformed into neutral amine.



If the valency isomeric Hantzsch-Werner formulæ are used, each of the tautomeric formulæ may also be written for the free base, the salt, etc., but the red form does not appear by its structure to be necessarily the stronger base.

The complete equations expressing the electrical and tautomeric equilibria of amino-azo bases will consist of one expressing salt formation and hydrolysis of each tautomer, the hydration equation of the azoid base and three tautomeric equations of the base, kathion and salt, or six in all. If there is also a negative affinity centre on the molecule, the possible equilibria become more numerous, as in the case of the amphoteric methyl orange. The question whether the acid or basic character predominates in different cases has given rise to much discussion, and may be illustrated by the example of methyl orange (Waddell, *J. Chem. Soc.*, 522 (1913)).

The free helianthin is easily soluble in alkalies giving well defined salts. The sodium salt, methyl orange, is not hydrolysed even in dilute solution (Tizard, p. 145).

On the other hand, it is only very slightly soluble in acids. About 6·2 c.c. of $\frac{1}{163}$N. HCl produce a turbidity in 100 c.c. of $\frac{1}{2\,6\,5}$N. methyl orange (Winkelblech, *Zeitsch. phys. Chem.*, 36, 573 (1901)). It does not easily form a hydrochloride. According to Hantzsch this salt can be prepared by crystallisation from hot concentrated hydrochloric acid, but this preparation when dry contains only 9 instead of 10·4 per cent. of HCl, and is very unstable (*Ber.*, 41, 1192 (1908)).

The conductivity does not give any evidence for salt formation in solution. Thus Winkelblech, above, finds that the conductivity of HCl is scarcely affected by shaking with red solid helianthin. The red form when dissolved in acid is not a kathion but an amphoteric ion or inner salt, since the boundary between an acid solution coloured with helianthin and one uncoloured does not move in an electric field of force. In an alkaline or weakly acid solution the coloured boundary moves towards the anode (Kremann, *Zeitsch. anorg. Chem.*, 33, 92 (1902)).

Other evidence is derived from the independent knowledge of the strength of the acid and basic centres. Since the presence of the centre of opposite polarity decreases the strength of each centre, therefore the strength of each centre when present alone on a neutral molecule is the upper limit of that to be expected from the same centre on an amphoteric molecule. Dimethyl amino-azo benzene is only a very weak base (Winkelblech, p. 137). Methyl red, the carboxylic acid, is still weaker, although according to the results of Tizard the basic constant is still appreciable (p. 147), and it forms salts with acids (Chap. III., p. 123). Helianthin with the more negative $HSO_3$ group may be expected to behave as a stronger acid. On all these accounts it is very probable that this indicator is an acid and not a base. The basic character, however, is manifested in the formation of an inner salt in strongly acid solution.

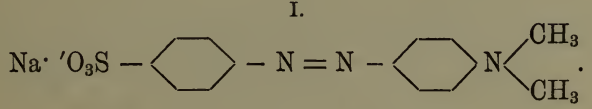
It has been said on the other hand that methyl orange is a basic indicator, because it undergoes the same colour changes as, *e.g.*, dimethyl amino-azo benzene (Kuster, *Jahrbuch der Chem.*, 7, 64 (1898)).

The statement that it is the basic centre of these compounds which really determines the colour changes is of course correct if the formulæ of Chap. III. are accepted. But the tautomeric changes can be represented by the same

kinds of interaction between the amino and azo groups, whether the salt formation takes place on an acidic or on a basic centre. Consequently the fact that amino groups are common to all diazo indicators is no proof that the salt is always formed on these groups. Similar interactions resulting in similar colour changes take place between other groups, *e.g.*, OH, etc., and the diazo group (see Chap. III., p. 119), so that in general it may be concluded that the necessary condition of the colour change is not a basic but an unsaturated character of the substituent groups.

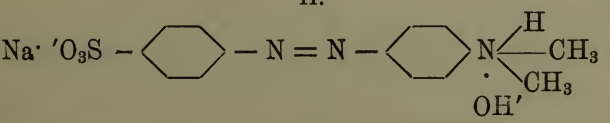
Each of the two tautomers of amphoteric amino-azo compounds may be present in any one of the following forms: Undissociated amphoteric compound [HMOH], anion 'MOH, kathion HM·, amphoteric ion or inner salt 'M· or —M—. The possibility of the existence of any of these in appreciable amounts depends upon the relative strength of the acid or basic centres. Methyl orange in alkaline or even in neutral solution is the salt of the sulphonic acid of azoid structure, and exists mainly as anion:—

I.



There is probably very little, if any, amphoteric ion

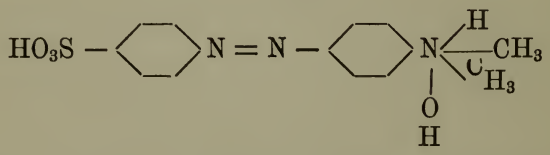
II.



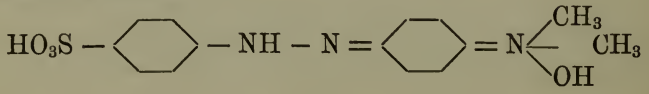
on account of the weakness of the basic centre. It seems reasonable on general grounds to assume that the tautomer which is favoured by the presence of alkalies is the weaker base.

The anion is in respect to its basic centre probably an amine or non-electrolyte I. above, on analogy with ammonia and the amines (see Chap. III., p. 107), or perhaps a pseudo base III. on analogy with the triphenyl methane compounds.

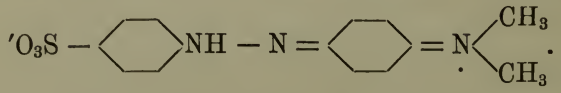
III.



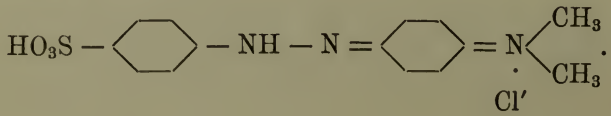
It is also to be expected that the basic centre will have its maximum strength in the red form which is favoured by acids. The free acid helianthin in aqueous solution contains about 10 to 20 per cent. of the red tautomer (Hantzsch, quoted by Thiel, "Indikatoren"). The red form is probably present chiefly as



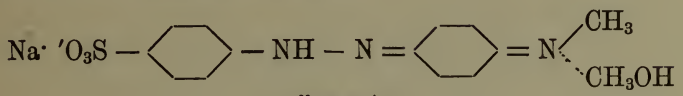
or rather as amphoteric ion formed from this by dehydration.



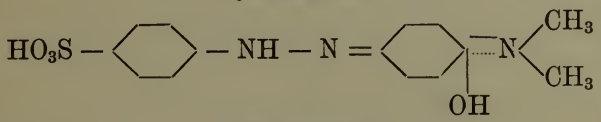
The loss of a negative electron to H· with attachment of the atom to the acid group and the formation of a kathion or salt occurs only with great difficulty if the acid radicle is as strong as $HSO_3$.



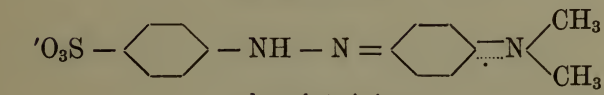
These changes can of course also be represented by the valency tautomeric scheme



yellow anion.

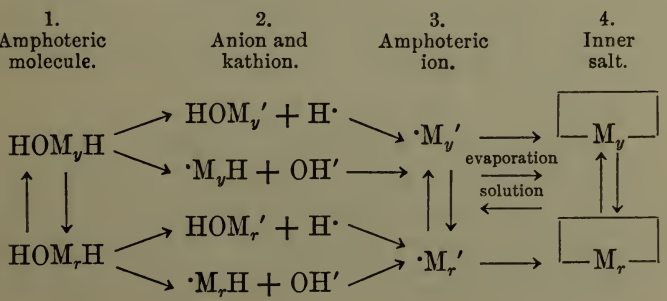


red molecule.



red amphoteric ion.

The precise nature of the tautomeric changes may well be left open when electrolytic equilibria are being considered. The formulæ may then be written $HM_yOH$ (yellow) and $HM_rOH$ (red) in which $M_y$ and $M_y$ are the residues from the dehydration of the hydrated molecules. All possible forms are given below except the amino acid, which is produced in the azoid quinoid scheme by the dehydration of $1_y$ in such a way that OH and H are both taken from the same amino nitrogen.




The horizontal and inclined arrows represent electrolytic

or hydration equilibria which are directly affected by change of [H·] and by loss or gain of water. The vertical arrows represent the tautomeric equilibria. In the absence of any knowledge of the separate constants it is only possible to say that those ions, etc., which would be formed in the presence of acids must have a high ratio red to yellow. The Noyes theory (see p. 129) may be applied to these equilibria.

Acids tend to produce kathion, or in this case amphoteric ion, therefore the ratio $\cdot M'_r/\cdot M'_y$ must be high. So, also, in the case of solid helianthin $\overline{|—M_r—|}$ must be the stable form. And similarly the anion equilibrium is far displaced towards the yellow form. These arguments have been stated in a more general form by Thiel, "Indikatoren."

Since all the equilibria in each horizontal row are connected with one another directly or indirectly, the concentration of each electro-chemical species (anion, inner salt, etc.) must be a continuous function of [H·]. The constants of the equilibria between the two tautomeric forms must be different in the case of different electro-chemical species as shown above, *e.g.*, in the case of the anion and kathion. Because, if the tautomeric constants were all the same a variation in [H·], and therefore in the relative amounts of the different electro-chemical species could produce no variation in colour.

### *The Determination of Indicator Constants.*

*The Colorimetric Constant found by Simultaneous Observations of* [H·] *and Colour.*—Solutions of different and known [H·] within the range of the indicator are prepared from the standards of Chap. V., and the amount of indicator in the coloured form is determined by a colorimeter or spectrophotometer. Clearly the method is most applicable

to a one-coloured indicator, but sometimes to a two-coloured indicator also (see p. 145, Tizard). Thus phenolphthalein was added by McCoy, *Amer. Chem. J.*, 31, 53 (1904) to mixtures of $NH_4Cl$ and $NH_4OH$ and the fraction of red form present was found colorimetrically (Acree, *Amer. Chem. J.*, 39, 539 (1908): Schugowitsch and Wegscheider, *Zeitsch. Electrochem.*. 14, 510 (1908); Hildebrand, *Zeitsch. Electrochem.*, 14, 349 (1908); Brode and Lange, *Kais Gesundheitsamt*, 30, 1 (1909); Fresenius, *Zeitsch. phys. Chem.*, 80, 481, (1912); Rosenstein, *J. Amer. Chem. Soc.*, 34, 1117 (1912); 35, 1883 (1913).

The results of Rosenstein are given in the table—

| [H·]. | $-\log$ [H.]. | $\frac{x}{1-x}$ found. | K. | $-\log K. = p_I$ | $\frac{x}{1-z}$ calculated. |
|---|---|---|---|---|---|
| $1{\cdot}13 \times 10^{-10}$ | 9·95 | 2·36 | $2{\cdot}37 \times 10^{-10}$ | 9·63 | 2·28 |
| $1{\cdot}33 \times 10^{-10}$ | 9·95 | 2·22 | 2·23 | 9·65 | 2·28 |
| $2{\cdot}26 \times 10^{-10}$ | 9·65 | 1·03 | 2·08 | 9·68 | 1·03 |
| $2{\cdot}93 \times 10^{-10}$ | 9·53 | 0·744 | 1·94 | 9·71 | 0·77 |
| $2{\cdot}96 \times 10^{-10}$ | 9·53 | 0·766 | 2·02 | 9·70 | 0·76 |
| $3{\cdot}42 \times 10^{-10}$ | 9·47 | 0·691 | 2·10 | 9·68 | 0·64 |
| $4{\cdot}41 \times 10^{-10}$ | 9·36 | 0·474 | 1·86 | 9·73 | 0·46 |
| $4{\cdot}65 \times 10^{-10}$ | 9·33 | 0·449 | 1·86 | 9·73 | 0·43 |
| $6{\cdot}70 \times 10^{-10}$ | 9·17 | 0·277 | 1·66 | 9·78 | 0·266 |
| $8{\cdot}06 \times 10^{-10}$ | 9·09 | 0·218 | 1·56 | 9·81 | 0·207 |
| $8\,82 \times 10^{-10}$ | 9·05 | 0·184 | 1·44 | 9·84 | 0·182 |
| $10{\cdot}9 \times 10^{-10}$ | 8·96 | 0·111 | 1·08 | 9·97 | 0·133 |

The figures of the third column give the fractional amounts of the coloured form, those of the fourth column the colorimetric constant calculated from these by the equation of a binary dissociation (Chap. I., p. 20). The drift in this constant suggests that the behaviour of phenolphthalein may be represented better as that of a dibasic acid.

In accordance with this idea (Wegscheider, Rosenstein) the colorimetric change may be represented by the equation—

$$\frac{[A'']}{[HA']+[H_2A]}=\frac{x}{1-x}$$

in which only the divalent ion is considered to be coloured.

Then by introducing the first and second dissociations of the acid it may be shown that—

$$[H\cdot]([H\cdot]+K_1)\frac{x}{1-x}=K_1K_2.$$

The figures in columns 1 and 3 give, as the mean value of the constants—
$K_1 = 11{\cdot}5 \times 10^{-10}$ $K_2 = 2{\cdot}825 \times 10^{-10}$ and from these the values of $\frac{x}{1-x}$ in column 6 were calculated.

These results were confirmed by the use of the distribution ratio of the colourless acid $H_2In$ between benzene and water (= 13·1).

For most purposes, however, the colour change is calculated with sufficient accuracy if phenolphthalein is taken as a monohydrion acid with an exponent equal to 9·7.

In the case of two-colour indicators the amounts transformed are separately proportional to the colour due to each form expressed as a fraction of the extreme colour of the solution when completely transformed in one or the other direction. The intermediate colour of each form is confused by the presence of the other form, which often makes the colorimetric estimation more difficult than in the case of a one-colour indicator. The actual intermediate colour of methyl orange, however, can quite well be defined in terms of the yellow colour of the completely ionised sodium salt which reaches a limiting value with only a slight excess of sodium hydroxide. There is, in fact, con-

siderable similarity between the absorption spectra of the two colours (see Chap. III., p. 122).

A colorimetric match may, therefore, be obtained between a red and a yellow solution of methyl orange by sufficiently decreasing the thickness of the latter. This observation was applied by Veley to the determination of the dissociation constants of some weak acids and bases (*Proc. Chem. Soc.*, 22, 213 (1906); 23, 284 (1908)).

Conversely Tizard, *J. Chem. Soc.*, 97, II., 2477 (1910), by measuring the relative colour of solutions of known [H·] has determined the constant of this indicator. The heights of a standard, weakly acid, methyl orange solution were found which were colorimetrically equal to those of the solutions to be investigated, which had the same methyl orange concentration, *i.e.*, N/20,000. The numerical values of these heights are then proportional to the absolute colours of the solutions. In order to calculate the amount transformed it is necessary to know the relative colour of the completely alkaline and completely acid solutions of the same strength. The weaker of these two colours is that of the fully ionised solution of the sodium salt. It was shown that after a dilution of 8,000 litres per mol had been reached a further dilution did not affect the colour. The solution is therefore fully ionised at these dilutions. The constancy of the colour also showed the absence of hydrolysis, which was further confirmed by the observation that the addition of a few drops of sodium hydroxide solution did not alter the colour.

All colours were, therefore, referred to this as unit through the standard solution of variable height, *i.e.*, the height of the latter solution $h$, which balances the ionic colour of the sodium salt, is taken as the standard height. If the corresponding height for a completely acid solution containing the same concentration of methyl orange is $h_u$, then

$h_u/h_i = C_u$ is the total increase of colour for the complete change. It was found that $C_u = 18{\cdot}8$. Now if $h_x$ is the height which balances a solution in which the fraction $x$ of the indicator has been changed into the red form,

$$\frac{h_x}{h_i} = C = \text{relative increase in colour due to } H^{\cdot}.$$

And separating the total colour into a part due to the red and to the yellow form

$$h_x = h_u x + h_i\,(1 - x)$$

Dividing throughout by $h_i$

$$C = C_u x + 1 - x.$$

$$\text{Whence } x = \frac{C - 1}{C_u - 1} \qquad 1 - x = \frac{C_u - C}{C_u - 1}$$

$$[H^{\cdot}] = K_A \frac{x}{1 - x} = K_A \frac{C - 1}{C_u - C} = K_A \frac{(C - 1)}{18{\cdot}8 - C}.$$

The values of $[H^{\cdot}]$ in the dilute HCl used were corrected where necessary for the undissociated methyl orange.

The mean value of K from a series of measurements was found to be—

$$4{\cdot}25 \times 10^{-4} \text{ at } 25°,$$

being in good agreement with that of Salm at 18° (see p. 149).

The colours calculated by the aid of this constant agreed with those observed to about $\pm$ 3 per cent. The concentration of the HCl was varied between N/20 and N/100,000. There is little change of colour between $[H^{\cdot}] = 1 \times 10^{-7}$ and $[H^{\cdot}] = 1 \times 10^{-5}$. The change is then rapid up to $[H^{\cdot}] = 1 \times 10^{-2}$, and after this point the colour increases by about 5 per cent. in more acid solutions. Methyl

orange, then, is found to be a suitable indicator for colorimetric determinations of acidity between $[H^{\cdot}] = 1 \times 10^{-3}$ and $[H^{\cdot}] = 1 \times 10^{-5}$. Since the colour remains unchanged up to N/20 acid solutions the basic constant is at any rate less than $1 \times 10^{-14}$.

*Methyl Red.*—$N(CH_3)_2 \cdot C_6H_4 \cdot N : N \cdot C_6H_4\,COOH$.

The colorimetric ionisation constant was measured in a manner similar to that just described. The potassium salt hydrolyses in moderately dilute solution depositing the slightly soluble acid. Since a clear neutral solution could not be prepared a very dilute solution of the acid itself was taken as the standard. A saturated solution of the acid showed an increase of colour with increasing $[H^{\cdot}]$. The lower acidities were obtained with acetic acid, sodium acetate $[H^{\cdot}]$ regulator (see Chap. V., p. 191), the higher with HCl. With N/5,000 to N/2,000 HCl the colour was at a maximum and 25·6 times the ionic colour. The curve up to this maximum is that of an acid with $K = 1{\cdot}05 \times 10^{-5}$. But in HCl concentration over N/2,000 the colour begins to decrease again, and this was explained by the appearance of the basic function.

This part of the curve has the same form as that of an amphoteric electrolyte. The constant $K_B$ was found to be $3 \times 10^{-13}$ and the relative colour of the kathion 18·6.

With HCl concentrations between N/5,000 and N/2,000 part of the molecule is present both as anion and kathion. A correction may be introduced for this, and the relative colour of the undissociated molecule is then found to be 27·6. The curve shows that methyl red is a sharper indicator than methyl orange, and its principal change occurs between 5·7 and 7·0. If it is used in a colorimeter to determine $[H^{\cdot}]$ the maximum colour is best taken as the standard of reference, since in this part of the curve

errors in preparing the required [H·] only affect the colour slightly. If C is the relative colour observed,

$$\text{Then } [H\cdot] = \frac{1{\cdot}05 \times 10^{-5}(C - 1)}{27{\cdot}6 - C}.$$

*Indicator Constants by the Method of Half-way Change.*

The colorimetric constant of an indicator can be determined, although less exactly, from one measurement only, and that value of [H·] is conveniently chosen at which the indicator change has proceeded exactly half-way. At this point K = [H·] (see Chap. I., p. 13).

In the experiments of Salm, *Zeitsch. phys. Chem.*, 57, 471 (1907), the [H·] was determined from the E.M.F. of the combination—

| | | | |
|---|---|---|---|
| $H_2Pt$ | HCl and 0·1 N·NaCl [H·] = 0·01 | Indicator solution 0·1 N·NaCl [H·] = K | $H_2Pt$ |

The NaCl was introduced in order to eliminate diffusion potential.

The half-way colour is found by the optical superposition of a solution containing the indicator completely changed in one direction, on a solution containing the same concentration of the same indicator completely changed in the other direction. The constants found will, of course, include the effect of the neutral salt.

The apparatus used for the colorimetric part of the experiment is similar to that described by Walpole, *Biochem. J.*, V., 213 (1910).

Two Nessler tubes, one containing, *e.g.*, a completely red solution of methyl orange, the other a completely yellow solution of the same indicator, are so placed in a colorimeter that the light reflected from a milk glass plate shines through both. They are matched by eye against

a tube of double the length and containing the same total amount of methyl orange. The colour of the latter is adjusted to equality with the half-way tint by the addition of small amounts of acid or alkali, and the [H·] measured as above.

The results should be compared with others in Table I., p. 155.

*Methyl Orange.*—$[H\cdot] = K = 4{\cdot}6 \times 10^{-4}$.

A value had been previously obtained by Winkelblech, *Zeitsch. phys. Chem.*, 36, 576 (1901), who measured the conductivity of super-saturated solutions of helianthin in water at 25°, $\Lambda_0$ being taken as 349.

The constant found was $3 \times 10^{-5}$.

Salm's value has also been confirmed by Tizard's results given above. Methyl orange, therefore, behaves colorimetrically as an acid about 25 times as strong as acetic acid.

*Dimethyl amino azo benzene.*—The value of [H·] at the half-way tint is $7{\cdot}0 \times 10^{-4}$. It behaves, therefore, as a moderately strong acid. It is really a base, however, and the basic constant corresponding to this value of [H·] is

$$\frac{K_W}{K_A} = 1{\cdot}0 \times 10^{-11}.$$

*Paranitrophenol.*—By means of the conductivity Bader* found $K_A = 1{\cdot}2 \times 10^{-7}$.

Salm attributed his first value $K_A = 3{\cdot}4 \times 10^{-9}$ to a reduction of the $NO_2$ group by the hydrogen. By shortening the time of contact with the gas, he found $K_A = 2{\cdot}3 \times 10^{-7}$.

*Rosolic acid* and *alizarin* were also measured with the results given in the Table I., p. 156.

*Phenolphthalein.*—$K = 8{\cdot}0 \times 10^{-10}$.

The result differs rather widely from those of other

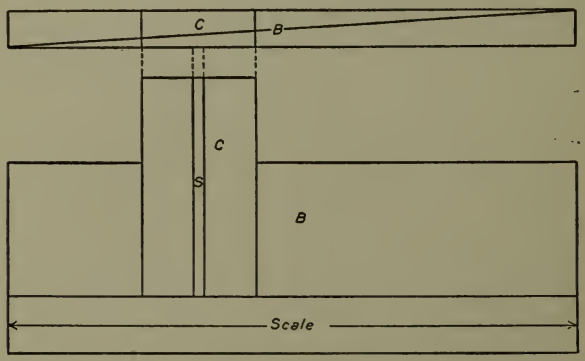
* *Zeitsch. phys. Chem.*, 6, 297 (1890).

experimenters. McCoy gives $1{\cdot}3 \times 10^{-10}$ and Hildebrand $1{\cdot}7 \times 10^{-10}$. The former measured the degree of hydrolysis of the indicator salt colorimetrically, the latter with the spectrophotometer. Wegscheider, using a similar method to McCoy, gives $1{\cdot}76 \times 10^{-10}$ at 23°. A discussion on the best constant for this indicator has already been given, p. 144.

*Cyanin.*—$[H^{\cdot}] = 2{\cdot}4 \times 10^{-9}$ $[OH'] = 4{\cdot}2 \times 10^{-6}$

$K_B =$ ,, ,,

Many indicators cannot be investigated in this way




Wedge Colorimeter for Measuring the Degree of Transformation of Indicators.

because other changes set in before the full acid or alkaline colour is produced by change of $[H^{\cdot}]$, or the production of the extreme colour or colours may be followed by a rapid fading. Where applicable, however, the method is simple and satisfactory for two-colour indicators.

*The Colour Wedge Device.*—A considerable extension of this method due to Bjerrum (preface) enables a series of transformation ratios of two-colour indicators to be measured as readily as those of a one-colour indicator with

an ordinary colorimeter. A rectangular box with glass sides, about 30 cm. long, 10 high, and 2 thick, is divided into two wedge-shaped compartments by a diagonal piece of glass. The two compartments are filled (1) with the indicator completely transformed by acid, (2) with indicator of the same concentration completely transformed by alkali. A cell C containing the same concentration of indicator partly transformed by a known [H·] is then brought vertically above B, and the position is found at which the colour of C is exactly the same as that of a narrow strip S of B. This position may be read on a scale placed behind, or traversed by a pointer from S, etc. Some measurements with methyl orange are quoted, from which the constant is found to be $2{\cdot}5 \times 10^{-4}$, which is thus lower than those determined by Salm, $4{\cdot}6 \times 10^{-4}$, or Tizard, $4{\cdot}25 \times 10^{-4}$.

The discrepancy may be accounted for by the fact that Tizard, using a series of measurements, was able to obtain by extrapolation the limiting value of the red colour when [H·] is indefinitely increased, which was then introduced into the calculation of the amount transformed.

On the other hand, in the simple apparatus sketched above, it is assumed that the indicator can be converted into the red form by a moderate amount of acid. If the conversion is incomplete, then at a given value of [H·]

$K = \frac{[H\cdot]\ \text{yellow}}{\text{red}}$ will be returned at a lower value than the true one.

Thus Bjerrum finds that at $-\log [H\cdot] = 3$ the percentage of red is 80; while from the formula

$$\frac{x}{1-x} = \frac{\text{red}}{\text{yellow}} = \frac{10^{-3}}{4{\cdot}25 \times 10^{-4}} \text{ and } x = 70 \text{ per cent.}$$

The agreement of Salm's constant with that of Tizard rather than with that of Bjerrum, although found by a

method essentially the same as the wedge device, may possibly be attributed to the presence of sodium chloride (see section on neutral salt action).

Still further variations are possible in the methods of determining indicator constants, since the two data, the [H·] of the solution and the fraction of indicator transformed, can each be found in several ways. A simple procedure is to titrate until the colour is seen to change and then to measure [H·] with the hydrogen electrode. In this way approximate values of [H·] at the change point are found. The method was used by Salessky. Or the colour change may be produced by regulator mixtures (see Chap. V.), of which [H·] may be calculated according to the methods given below.

Fels, who used solid orthophthallic acid and sodium hydroxide as a regulator (see Chap. I., p. 40), followed the colour change spectroscopically and obtained the results quoted in Table I., pp. 155, 156. The [H·] corresponding to various tints may also be found from the number of c.c. of acid or alkali required to produce the intermediate tint. Thus Kuster and Gruters, *Zeitsch. anorg. Chem.*, 35, 454 (1903), find that 50 c.c. of an aqueous solution of methyl orange is turned to an orange colour by 0·03 c.c. of 0·1 N.HCl, red by 0·05 c.c. Hence $-\log$ [H·] for the half-way change (orange) is 4·22 ($= p_I$, see p. 164), and for a decided red, 4·0.

Another method which has been used by H. C. Jones and his collaborators (*Reports of the Carnegie Institution*, 230 (1915)) to find the degrees of transformation of some indicators, is the determination of the total absorptions (at wave lengths where the selective absorptions due to the indicators are considerable) by means of a very delicate thermo junction. This consisted of a thin wire loop having a tinfoil blackened receiver with a mirror, and a compensation

for stray radiations. The total weight of the compensated thermo junction was 2·9 mgms. The absorptions of the cell, etc., were eliminated by measuring a depth of 21 mm. and then 1 mm. of the same solution. If I and I′ are the intensities of the radiation transmitted through these depths, then it can be shown that $\log \frac{I}{I'}$ is the true constant of absorption for 20 mm. of the solution.

In order to determine the concentrations of each differently absorbing form from the total absorptions and concentrations, it is necessary to know the absorption constants $K_1$ and $K_2$ of the forms 1 and 2. From solutions of the indicators which have been completely transformed in the manner already mentioned, values of

$$\log \frac{I_1}{I_0} = -K_1C \text{ and } \log \frac{I_2}{I_0} = -K_2C$$

may be determined (see Chap. II., p. 70).

Now if I is the intensity of light transmitted when $C_1$ is present as 1 and $C_2$ as 2,

$$\log \frac{I}{I_0} = -(K_1C_1 + K_2C_2) \text{ and } C = C_1 + C_2$$

$$\therefore \log \frac{I}{I_0} = -K_1C_1 - K_2C + K_2C_1$$

or
$$C_1 = \frac{K_2C + \log \frac{I}{I_0}}{K_2 - K_1},$$

and putting in place of $K_1$, etc., the experimental log ratios for 20 cm. of solution,

$$C_1 = \frac{C\left(\log \frac{I}{I_0} - \log \frac{I_2}{I_0}\right)}{\log \frac{I_1}{I_0} - \log \frac{I_2}{I_0}}$$

In the case of a one-colour indicator ($C_2$ does not absorb), the corresponding equation is

$$\frac{C_1}{C} = \log \frac{I}{I_0} \Big/ \log \frac{I_1}{I_0}$$

The absorption of phenolphthalein ($C = 5$ to $3{\cdot}5 \times 10^{-5}$ mols.) was measured at $\lambda = 577{\cdot}3$, $579{\cdot}8$, $582{\cdot}3$, $584{\cdot}8$ and $594{\cdot}7$ (see diagram VI., p. 339) in solutions of varying ($OH'$) derived from $NH_4Cl$ and $NH_4OH$ mixtures.

The values of K for the indicator considered as a monohydrion acid were found to decrease as [H·] increases as in the results of Rosenstein (p. 143). The constant of methyl orange ($C = 1$ to $2 \times 10^{-4}$ mols.) in dilute $H_2SO_4$ ($C = 1 \times 10^{-6}$ to $1 \times 10^{-4}$) was found by the same method to be $5 \times 10^{-4}$.

Rosolic acid was investigated by Paulus and Hutchinson. In dilute alkaline solution [NaOH] = 0·005 to 0·03, the transmission ($\lambda = 560$ to $580$) gradually decreased, reaching a constant value in from 1 to 5 hours. This time effect was noticed up to the neutral point, but on the acid side of this, equilibrium is more quickly attained. With higher alkali concentration ($C = 0{\cdot}1$) the colour gradually fades. If the constant is calculated as that of a monohydrion acid, it falls from $5{\cdot}65 \times 10^{-8}$ to $2{\cdot}89 \times 10^{-8}$ as $10^8$ [H·] increases from 2·5 to 19·5. If it is considered as a dihydrion acid, the ratio $[Mr]/[My]$ (see p. 142) can be expressed at various functions of [H·], $K_1$, $K_2$, according as it is assumed that the primary and secondary ions $HM'$ and $M''$ have the same or different colours. The agreement with experimental results is best when it is assumed that both $M'$ and $HM''$ are red ($H_2M$ yellow).

In this case

$$\frac{[M_r]}{[M_y]} = \frac{[H\cdot]\,K_1 + K_1K_2}{[H\cdot]^2}$$

| | | | | |
|---|---|---|---|---|
| $10^8\,[H\cdot] =$ | 2·535 | 4·484 | 10·53 | 19·52 |
| $\frac{[M_r]}{[M_y]}$ observed $=$ | 2·23 | 1·12 | 0·371 | 0·148 |
| $\frac{[M_r]}{[M_y]}$ calculated $=$ | 2·23 | 0·95 | 0·308 | 0·148 |

## TABLE I.

### Indicator Constants.

| Indicator. | Indicator Exponent or Range. | Concentration, Colour Change and other Remarks. |
|---|---|---|
| Mauvein | — 0·3 ⟶ 2·5 | Salm |
| Methyl violet | 2·7 ⟶ 3 | Colourless ⟶ dark blue (Salessky). |
| | 2·05 ⟶ 2·4 | Blue ⟶ violet (Fels). |
| | 3 | Blue-green ⟶ violet, 0·1 per cent. in water. |
| | 1 — 2 | Yellow ⟶ green, 0·1 per cent. in water (Michaelis). |
| Tropaolin 00 | 1·3 ⟶ 2·4 | Pink ⟶ yellow (Michaelis). |
| Methyl orange | 2·7 ⟶ 5·4 | 0·25 to 0·001 millimols/litre |
| | | 0·1 c.c. of 0·003, or 0·8 per cent. solution to 10 c.c. (Salessky and Fels). |
| | 4 | 0·1 c.c. of 0·1 per cent. to 100 c.c. (Bjerrum). |
| For | other values, see | pp. 146, 149. |
| Sodium sulphalizarate | 3·7 ⟶ 4·2 | Yellow ⟶ pink (Michaelis). |
| Methyl red | 5·5 | Red ⟶ yellow, 0·1 c.c. of 0·1 per cent. to 100 c.c. (Bjerrum). |
| | 5 | 0·5 per cent. in 90 per cent. alcohol (Michaelis). |
| | See also Tizard's | results, p. 147. |

TABLE I.—INDICATOR CONSTANTS—*continued.*

| Indicator. | Indicator Exponent or Range. | Concentration, Colour Change and other Remarks. |
|---|---|---|
| Litmus | 5 ⟶ 8 | Red ⟶ violet ⟶ blue (Salessky). |
| | 6 ⟶ 7 | Blue - red ⟶ red - blue, 1 c.c. of 2 per cent. solution of extract to 100 c.c. (Bjerrum). |
| | 6·8 | Usual solution (Michaelis). |
| Rosolic acid | 6 ⟶ 7 | Brown ⟶ pink, 1 c.c. of 0·1 per cent. to 100 c.c. (Bjerrum), see also p. 154. |
| | 7·96 | Half-way tint (Salm). |
| Phenol-phthalein | 8 | 0·7 c.c. of 1 per cent. in alcohol to 100 c.c. (Bjerrum). |
| | 9 | 0·4 c.c. of 0·1 per cent. to 100 c.c. |
| | 8·4 ⟶ 9·2 | $p_T$ (Noyes). |
| | 9 | 1 per cent. in 90 per cent. alcohol (Michaelis). |
| For | other values, see | pp. 144, 154. |
| Para-nitrophenol | 7·0 | Alcoholic solution. |
| | 4·0 ⟶ 6·5 | $p_T$ (Noyes). |
| | 6·13 ⟶ 6·75 | Colourless ⟶ yellow (Fels). |
| | 6 | 1 per cent in 90 per cent. alcohol (Michaelis). |
| Tropaolin 000 | 8 ⟶ 11·22 | Yellow ⟶ orange ⟶ red (Salessky-Fels). |

TABLE II.

INDICATOR CONSTANTS. Sorensen's List.

| Indicator. | Exponent or Range. | Concentration, Colour Change and other Remarks. |
|---|---|---|
| Methyl violet | 0·1 ⟶ 1.5 | 3 to 8 drops to 10 c.c. 0·05 per cent. |
| ,, ,, | 1·5 ⟶ 3·2 | 10 to 4 ,, ,, 0·01 ,, |
| Mauvein | 0·1 ⟶ 1·5 | 3 to 8 ,, ,, 0·05 ,, |
| ,, | 1·5 ⟶ 2·9 | 4 to 10 ,, ,, 0·01 ,, |
| Benzene azo diphenylamine | 1·2 ⟶ 2·1 | 6 to 15 ,, ,, 0·01 ,, |
| P. benzene azo diphenylamine sulphonic acid (tropaolin 00) | 1·4 ⟶ 2·6 | 3 to 5 ,, ,, 0·01 ,, |
| The meta compound (metanil yellow) | 1·2 ⟶ 2·3 | 3 to 5 ,, ,, 0·01 ,, |
| Benzene azo benzyl aniline | 2·3 ⟶ 3·3 | 5 to 10 ,, ,, 0·02 ,, |
| Benzene azo benzyl aniline p. sulphonic acid | 1·9 ⟶ 3·3 | 3 to 6 ,, ,, 0·01 ,, |
| P. benzene sulphonic acid azo meta chlor diethyl-anili | 2·6 ⟶ 4·0 | 3 to 5 ,, ,, 0·01 ,, |
| Benzene azo dimethylaniline | 2·9 ⟶ 4·0 | 5 to 10 ,, ,, 0·01 ,, |
| P. benzene sulphonic acid azo dimethylaniline (methyl orange) | 3·1 ⟶ 4·4 | 3 to 5 ,, ,, 0·01 ,, |
| Benzene azo and naphthylamine | 3·7 ⟶ 5·0 | 10 to 20 ,, ,, 0·01 ,, |
| P. benzene sulphonic acid azo α naphthylamine | 3·5 ⟶ 5·7 | 8 to 12 ,, ,, 0·01 ,, |
| O. benzene carboxylic acid azo dimethylaniline (methyl red) | 4·2 ⟶ 6·3 | 2 to 4 ,, ,, 0·02 ,, |
| P. nitrophenol | 5·0 ⟶ 7·0 | 3 to 20 ,, ,, 0·04 ,, |
| Neutral red | 6·8 ⟶ 8·0 | 10 to 20 ,, ,, 0·01 ,, |
| Rosolic acid | 6·9 ⟶ 8·0 | 6 to 15 ,, ,, 0·04 ,, |
| P. benzene azo α naphthol sulphonic acid (tropaolin 000, No. 1) | 7·6 ⟶ 8·9 | 4 to 10 ,, ,, 0·01 ,, |
| α naphtholphthalein | 7·3 ⟶ 8·7 | 4 to 12 ,, ,, 0·04 ,, |
| Phenolphthalein | 8·3 ⟶ 10·0 | 3 to 20 ,, ,, 0·05 ,, |
| Thymolphthalein | 9·3 ⟶ 10·5 | 3 to 10 ,, ,, 0·04 ,, |
| P. nitrobenzene azo salicylic acid (alizarin yellow) | 10·1 ⟶ 12·1 | 5 to 10 ,, ,, 0·01 ,, |
| P. benzene azo resorcin sulphonic acid (tropaolin 0) | 11·1 ⟶ 12·7 | 5 to 10 ,, ,, 0·01 ,, |

TABLE III.

APPROXIMATE COLOUR CHANGES OF INDICATORS.

| Indicator. | $[H^{\cdot}]=2$<br>$-\log[H^{\cdot}]=0{\cdot}3$ | 1<br>0 | $10^{-1}$<br>1 |
|---|---|---|---|
| Benzo purpurin B | blue | blue-violet | |
| Iodeosin | green-yellow | pink | |
| Mauvein | yellow | green | green-blue |
| Methyl violet | yellow | yellow-green | green-blue |
| Neutral red | blue | blue-violet | crimson |
| Benzaldehyde green | — | yellow-brown | green |
| | $-\log[H^{\cdot}]=1$ | 2 | 3 |
| Benzaldehyde green | green | blue | — |
| Mauvein | green-blue | blue | violet |
| Methyl violet | green-blue | blue | violet |
| „ (Michaelis) | yellow-green | blue-green | violet |
| Dimethylamino-azobenzene | — | crimson | flesh-colour |
| Tropaolin 00 | crimson | flesh-colour | yellow |
| | $-\log[H^{\cdot}]=3$ | 4 | 5 |
| Gallein | yellow | orange | red |
| Congo | blue | violet | scarlet |
| Methyl orange | orange-red | orange | yellow |
| Benzo purpurin B | red-violet | pink | yellow |
| Dimethylamino azo-benzene | flesh-colour | yellow | — |
| Sodium sulphalizarate | — | yellow-green | brown |
| Methyl red | — | red | yellow |
| | $-\log[H^{\cdot}]=5$ | 6 | 7 |
| Phenacetolin | brown-red | pink | — |
| Sodium sulphalizarate | brown | red | — |
| Alizarin | — | brown-yellow | lilac |
| Paranitrophenol | — | greenish | green-yellow |
| Rosolic acid | — | brownish | pink |
| Litmus | — | pink | violet |
| Cochineal | brown-pink | lilac | — |
| | $-\log[H^{\cdot}]=7$ | 8 | 9 |
| Litmus | violet | blue | — |
| Cyanin | pale blue | violet-blue | — |
| Neutral red | rose--pink | orange | — |
| Rosolic acid | pink | red | — |
| Phenolphthalein | — | pale pink | bright pink |
| Tetrabrom-phenol-phthalein | — | colourless | violet |
| α-naphthol-phthalein | reddish | greenish | blue |
| Alizarin | pale lilac | lilac | — |

TABLE III.—APPROXIMATE COLOUR CHANGES OF INDICATORS—*continued.*

| Indicator. | Exponent and Colour. | | |
|---|---|---|---|
| | $-\log[H^{\cdot}]=9$ | 10 | 11 |
| α-naphthol benzoin | brown-yellow | green | green-blue |
| Phenolphthalein | bright pink | crimson | — |
| Thymolphthalein | — | colourless | blue |
| Gallein | — | red | blue-violet, then brown |
| | $-\log[H^{\cdot}]=11$ | 12 | 13 |
| Poirrier's blue | blue | violet, then pink | — |
| Tropaolin 0 | green-yellow | orange | — |
| Alizarin | lilac | violet | — |
| Trinitrobenzene | — | colourless | orange |
| Phenacetolin | — | violet | colourless |
| | $-\log[H^{\cdot}]=13$ | 14 | 14·3 |
| Alizarin | violet | blue | — |
| Benzo purpurin B | yellow | pink | — |
| Gallein | blue-violet | blue | — |
| Mauvein | violet | violet-red | yellow-red |
| Trinitrobenzene | orange | red-orange | colourless |

*Indicators with Numerous Change-Points.*

Dinitrohydroquinine 2, 5.

Schuchardt's preparation twice recrystallised from water (Henderson and Forbes, *J. Amer. Chem. Soc.* 32,687 (1910)).

Solution 0·1 mol in alcohol.

| | | |
|---|---|---|
| Hydrion regulator | 0·1 tartaric | 0·058 $NaH_2PO_4$ |
| $-\log[H^{\cdot}]$ | 2 | 4 |
| Colour | Green-yellow | Orange-yellow |
| Hydrion regulator | 4 $NaH_2PO_4$ + 1 $NaH_2PO_4$ | 1 $NH_4OH$ to 27 $NH_4Cl$ |
| $-\log[H^{\cdot}]$ | 6 | 8 |
| Colour | Orange | Brown-red |

| | | |
|---|---|---|
| Hydrion regulator | 3·7 $NH_4OH$ to 1 $NH_4Cl$ | 1·0 N·$Na_2CO_3$ |
| $-\log[H^{\cdot}]$ . | 10 | 12 |
| Colour . . | Red-purple | Purple |

(See also Walpole, *Biochem. J.*, VIII., 6,631 (1914).)

Several other chameleon indicators suitable for rapidly finding the $[H^{\cdot}]$ of solutions have been included in Chapter VIII.

The advantages of mixed indicators are stated on p. 165.

The following are mostly derived from a paper by Scholtz.* The order of the colour changes clearly demonstrates that of the indicator exponents. The condition for a sharp titration is that these exponents should not be too far apart. The transition tint is very clearly marked if the difference is about 1 in the exponent, and this tint may be used as a warning that the titration colour (one of the extreme tints) has been nearly reached.

| Indicators. | Changes on the Addition of Alkali. | | |
|---|---|---|---|
| P. nitrophenol and rosolic acid . | pale yellow | intense yellow | orange |
| ,, and litmus . . | red | red-yellow | green |
| ,, phenolphthalein . | colourless | yellow | red |
| Rosolic acid and litmus . . . | orange | red | violet |
| ,, and α naphthol benzoin | yellow | pink | violet |
| Cochineal and litmus . . . | orange | red | violet |
| Phenacetolin and litmus . . | yellow-red | pink | violet |
| Dimethylaminoazo - benzene or methyl orange or tropaolin 00 . . . and cyanin | pink | yellow | green |
| Dimethylamino - azobenzene and litmus . . . . . | red | yellow-red | green |
| Congo and p. nitrophenol . . | blue | red | red-yellow |
| Congo and litmus . . . . | violet | red | violet |
| Cyanin and rosolic acid . . . | yellow | blue | violet |
| Cyanin and phenolphthalein . . | colourless | blue | violet |
| Sodium indigo sulphonate and methyl orange . . . . | violet | green to grey | yellow |

* *Zeitsch. Electrochem.*, 10, 549 (1904).

(Luther, *Chem. Zeit.*, 31, 1172 (1907); Kirschnick, *Chem. Zeit.*, 31, 960 (1907).)

A comparison of the constants referring to one and the same indicator (see Table I.) reveals some differences which must be attributed to variations in experimental conditions. The temperatures of different series vary between 18° and 25°.

The diffusion potentials in the hydrogen electrode experiments were not always completely removed. The change points of colour were determined sometimes by the unaided eye, sometimes by colorimetric or spectroscopic methods. The concentrations of the indicators also vary widely. Were all these conditions always carefully specified for each indicator constant, this could be used in colorimetric determinations of [H·] with considerable confidence.

Differences amounting to a whole unit or more in the hydrogen exponent, as in the case of tropaolin 000, must be ascribed to a want of uniformity in preparations sold under the same name.

On the whole the agreement of indicator constants found by different methods is good. It is therefore possible to make a rational classification of indicators on the basis of the hydrion function to which they owe their utility. This classification should replace the older subdivision into three classes—

(1) Insensitive to acids, sensitive to alkalies.

(2) Half-sensitive to acids and alkalies.

(3) Sensitive to acids, insensitive to alkalies.

It is evident that these classes correspond roughly to certain intervals of change points or exponents ( — log [H·] ).

(1) Between — 0·3 and 6.

(2) Between 6 and 8.

(3) Between 8 and 14·3.

A comparison of the lists (1), (2), and (3) given in Glaser's "Uber Indikatoren" with the tables shows that by the two methods of grouping the same indicators do indeed in the main fall into the same classes, if allowance is made for the difficulty of classifying those which are near the limits. Thus phenolphthalein will fall into the second or third class according to whether a high concentration and the palest pink tint or low concentration and a full red are taken as the change points.

The first group, according to Glaser, contains methyl violet, which behaves as a strong acid (actually a very weak base), also indicators of the amino-azo benzene type—tropaolin 00, methyl orange, ethyl orange, and dimethyl-amino-azo benzene. The inclusion of these as well as congo and benzo-purpurin is seen to be justified by the exponents. Intermediate between this and the next group are cochineal and lacmoid.

In the second group are several indicators—fluorescein, phenacetolin, and sodium sulphalizarate—which have practically the same constants as the last members of the first group. Alizarin, para-nitrophenol, and litmus are all typical neutral-point indicators. Gallein and hæmatoxylin are also included.

The third group contains the typical neutral-point indicator rosolic acid, as well as the acid sensitive tropaolin 000, phenolphthalein, curcumin, and $\alpha$ naphthol benzoin.

The advantages of classification according to constants or exponents will be evident from the graphical tabulation on the chart in the back cover, as also from the lists of change points at the head of the summary relating to each indicator. In the chart at the end only the most important changes or those most used in titrations, etc., are given. Others will be found under the summaries in Chap. VII.

The interval of $-\log [H^{\cdot}]$ over which the change occurs is stated in these cases. In Table II. above the change points are given only to 0·5 in $-\log [H^{\cdot}]$, which is nearest to the most marked colour change.

This degree of accuracy is quite sufficient for many purposes, *e.g.*, for the match method of Chap. V., or the titration of acids and bases which are not the very weakest.

The reproduction of the results of this table does not require a very exact attention to indicator concentration except in the case of a few one-coloured indicators, such as phenolphthalein, for which full details are given in Table I.

The change points of Salm refer to a constant concentration of 1 or 2 drops (or 0·1 c.c.) of a 0·1 to 0·15 per cent. solution of the indicator in water, alcohol, or a mixture added to 10 c.c. of solution.

Indicators of very intense colour, such as methyl orange, may well be used as 0·05 to 0·01 per cent. solutions. For ordinary titration purposes the concentrations may be much higher; thus a few drops of 1 per cent. phenolphthalein or 3·5 per cent. para-nitro-phenol in alcohol may be added to from 20 to 100 c.c. of solution.

The transition tints of indicators which change gradually, *e.g.*, litmus, are denoted by hyphens, *e.g.*, blue-red for bluish red.

At the end of Table III., p. 159, and in the lower part of the chart in the back cover, are placed some indicators which show a variety of change points and are useful for rapidly finding $[H^{\cdot}]$ (see Chap. V., p. 206).

*The Relation between Indicator Exponents and the Amounts of Colour.*

It is often convenient to characterise indicators by the negative exponent of the hydrion concentration (expressed

as a power of 10) at which the change has taken place to the extent of one-half. Calling this exponent $p_I$, then according to p. 13, since $x = 1 - x$, $10^{-p_I} = K$, or

$$p_I = -\log K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

And for another degree of transformation at another value of $-\log [H^+] = p$,

$$\log \frac{1-x}{x} = \log [H^+] - \log K = -p + p_I,$$

$$\text{or } p = p_I - \log \frac{1-x}{x} \quad . \quad . \quad . \quad . \quad . \quad (2a)$$

For a basic indicator with hydrogen exponent $p_I$,

$$p_I = \log K_B - \log K_W \quad . \quad . \quad . \quad . \quad . \quad . \quad (1b)$$

And from equation (2*b*), p. 133, in which $1 - x$ is now the kathion and $x$ the free base,

$$p = p_1 - \log \frac{1-x}{x}.$$

The degree of colour of an indicator solution is, then, exactly the same function of its colorimetric constant as the ionisation is of the electrometric constant, and the same equations may be used to determine the latter as the former (see Chap. I.). A graph may also be constructed of $a$ or $x$ against $-\log [H^+]$, which has exactly the same form for all values of K, but is displaced one way or another along the axis of abscissæ $-\log [H^+]$, according to the particular value of K. The graph or its equation serves to determine K from $x$ and $[H^+]$, or $x$ from K and $[H^+]$. It also gives the width or range of $[H^+]$ included in the transformation interval. The limits of visible change may be placed at a percentage transformation of 5 or 95. The greatest interval for a single change of an indicator at fixed concentration is therefore 2·56 units in $p_H$. It is evident

from Table I. that the observed interval is actually not greater than this even in the case where the indicator concentration is varied. Indicators such as methyl violet show a great variety of colours extending over a much wider interval of [H·], but the above theory only applies to one of such changes. Since these indicators are capable of forming polyvalent ions, their transformation curve, like the ionisation curve of, *e.g.*, phosphoric acid, will include two or more dissociation constants.

The wide interval for litmus (between 3 and 4 in $-\log [H\cdot]$) is probably due to the fact that this indicator is in reality a mixture of allied compounds.

A mixture of acids and bases with slightly different constants must always have a wider change-interval than a single indicator forming a monovalent ion.

For such a mixture behaves like an electrolyte which forms polyvalent ions, the chief difference being that the constituents of the mixture may be numerous and close together at will, while those of the acid or base which forms polyvalent ions are limited in number, and usually differ from one another in order of magnitude. A change-interval which includes more than one constant of a single indicator is therefore too large, while that produced by a mixture of indicators may be most suitable, although the change cannot be as sharp as for a single indicator unless the constants happen to be identical. The advantage of mixing indicators is that very marked changes of tint may be secured thereby. A conspicuous difference between the acid and alkaline colours is for most observers a great help, and is somewhat lacking in some two-colour indicators, such as those of the amino-azo group. The preference for an indicator like congo is probably founded mainly on the sharp contrast of colours, and the same reason accounts for the continued use of litmus in any titrations except those

of strong acids and bases. The particular advantages of two-colour indicators are further discussed on p. 165, and some mixtures are mentioned on p. 160 above.

*The Effect of Temperature upon Indicator Exponents.*

Since the heat of neutralisation of a weak acid by a strong base is less than that of a strong acid by a strong base, it follows that the heat of ionisation of the weak acid is negative. Therefore by thermodynamical reasons it can be shown that the dissociation constant of the weak acid (or equally, weak base) must increase with rise of temperature. If the heat of neutralisation, although less than that of the strong acid, is still positive, it also follows that the heat of ionisation of water is numerically greater than that of the acid, and therefore the water constant will increase more rapidly with rise of temperature than that of the acid. Hence the degree of hydrolysis of the indicator salt will also increase.

The degree of hydrolysis will also increase (*a fortiori*) if the constant of the indicator at some temperature below 100° reaches a maximum and then decreases, since it is known that the water constant does not reach its maximum until far above 100° (see Chap. I., p. 6).

A solution containing only an indicator salt should show a decrease in the salt colour with rise of temperature. If, however, the indicator is a moderately strong acid, *e.g.*, helianthin, then the hydrolysis should be so slight even at the higher temperature that no appreciable change of colour is produced. These conclusions have been partly tested by the work of Schoorl, *Chem. Weekbl.*, 3, 719, 771, 807 (1906); *Chem. Centralblatt*, I., 300, 502, 586 (1907); Bonnema, *Chem. Centralblatt*, II., 963 (1903); Hirsch, *Ber.*, 35, 2874 (1902).

With rise of temperature it was found that the yellow of

methyl orange and the red of congo remained unchanged; lacmoid changed from violet to blue, para-nitro-phenol to a deeper yellow, litmus and rosolic acid were unaltered, while phenolphthalein, which had been made first pink with alkali, became colourless. Thus phenolphthalein as a weak acid changes in the expected direction, and no change was to be expected from methyl orange and congo (and possibly litmus and rosolic acid), since the hydrolysis of the former will be too slight at any temperature.

If lacmoid is to be considered as a weak base it should change colour in the reverse direction. There should be no change, or perhaps a decrease, of colour in the case of para-nitro-phenol.

It is known, however, that the solution of the free acid in water also darkens on heating, and the same is true of the nitro-phenols in the solid state (Hantzsch, *Ber.*, 39, 1087 (1906)).

The effect is, then, probably due to a displacement of the tautomeric equilibrium, which masks the supposed opposite displacement of the electrolytic equilibrium. In the case of one-colour indicators, according to p. 130, the colorimetric constant need not be identical with the ionisation constant. The total effect of temperature upon the tautomeric, which are contained in the colorimetric, constants is unknown, so that clearly the colour change may not take place in accordance with the change of ionisation.

If other electrolytes besides the indicator salts are in solution, then the change of hydrolysis of the former will take place in the same direction as that of the latter, when a salt of a weak acid is present together with a salt of a weak acid indicator. Consequently when the mixture has a balanced $[H^{\cdot}]$ due to other electrolytes rather than to the indicator salts the colour changes on heating will in the case just quoted be the reverse of those given above. In

ordinary titrations and colour matching the effect of temperature on the [H·] produced by these is far more important than that on the indicator constant. The subject is continued in Chap. VI., p. 258.

*The use of Indicator Constants in determining the sensibility of Indicators and in the choice of the best Indicator Concentrations and Colours.*

The total problem of choosing an indicator for a given purpose may be divided into several parts.

(1) The choice of the indicator itself to suit the range of [H·] of the titration, etc. This is carried out with the aid of the tables already given, and is more fully dealt with in Chap. VI. The choice of the right indicator is pre-supposed in dealing with the succeeding questions.

(2) What is the useful range? In other words, at which part of the transition interval is the relative alteration greatest for a definite alteration in log [H·]?

(3) At which part of the transition interval is a given relative alteration most apparent to the eye?

(4) What is the best concentration of the indicator?

These questions will first be considered in relation to one-colour indicators.

(3) It has been found by comparing solutions the colours of which increase in a geometrical ratio, *e.g.*, 1, 2, $2^2$, $2^3$, that there is a considerable interval between the weakest and the strongest colour, over which the sensitivity of the eye to this relative change remains at a constant maximum. From the physiological point of view, then, it is only necessary to keep within this interval, and probably on the side of weaker colour.

It may be shown that the relative rate of increase $\frac{dx}{xd[\mathrm{H}\cdot]}$ of the coloured and ionised part $x$ of an indicator with

decrease of $[H^{\cdot}]$ is greater when $[H^{\cdot}]$ is much greater than K and smaller when $[H^{\cdot}]$ is much smaller than K. The converse holds for $\frac{d\,(1-x)}{(1-x)\,d\,[H^{\cdot}]}$.* It will be seen that the optimum ionic colour is to be found on the acid side of K, this colour being the weakest which can be conveniently perceived, for the weaker it is the greater is the relative change. The conditions of illumination, etc., and the personal equation count for so much here that it is often unnecessary to be more precise in specifying the exact value of $x$. The optimum colour, then, of an indicator acid with coloured ion will lie slightly on the acid side of $p_I$. If it is the molecule which is coloured then the converse holds, the optimum for an acid indicator will lie on the alkaline side and that for a basic indicator on the acid side of $p_I$. Or generally the best change point of a one-coloured or symmetrically-coloured indicator will lie in the less strongly coloured half of the transition interval. These relations have been expressed in a slightly different form, and experiments have been made to test their validity by Brode and Lange, *Arb. aus der Kaiserl. Gesundheitsamt*, 30, 1, 1909.

The total colour change will almost certainly be comprised between $10^3$ K and $10^{-3}$ K, but the range within which colorimetric measurements are possible will be more restricted. The fractional variation of the amount transformed with $[H^{\cdot}]$ differs in different parts of the interval. Thus from $[H^{\cdot}] = 10^3$ K to $[H^{\cdot}] = 10^2$ K the coloured part $x$ increases nearly ten-fold for a ten-fold decrease in $[H^{\cdot}]$; from $[H^{\cdot}] = 10^2$ K to $[H^{\cdot}] = 10$ K the colour increases nine-

* By differentiating $x = \frac{K}{K + [H^{\cdot}]}$ the relative decrease of $x$ with absolute decrease of $[H^{\cdot}]$ may be obtained

$$\frac{dx}{x} = \frac{d[H^{\cdot}]}{[H^{\cdot}]}\left(\frac{[H^{\cdot}]}{[H^{\cdot}] + K}\right).$$

| $[H^{\cdot}]$ | $x$ | $1-x$ | Per cent. as Ion. | Per cent. as Molecule. |
|---|---|---|---|---|
| $10^3$ K | $\frac{1}{1001}$ | $\frac{1000}{1001}$ | 0·0999 | 99·9 |
| $10^2$ K | $\frac{1}{101}$ | $\frac{100}{101}$ | 0·99 | 99·01 |
| 10 K | $\frac{1}{11}$ | $\frac{10}{11}$ | 9·1 | 90·9 |
| K | $\frac{1}{2}$ | $\frac{1}{2}$ | 50 | 50 |
| $10^{-1}$ K | $\frac{10}{11}$ | $\frac{1}{11}$ | 90·9 | 9·1 |
| $10^{-2}$ K | $\frac{100}{101}$ | $\frac{1}{101}$ | 99·01 | 0·99 |
| $10^{-3}$ K | $\frac{1000}{1001}$ | $\frac{1}{1001}$ | 99·9 | 0·0999 |

fold, from 10 K to K 5·6-fold, from K to $10^{-1}$ K 1·8-fold, from $10^{-1}$ K to $10^{-2}$ K 1·09-fold, and from $10^{-2}$ K to $10^{-3}$ K 1·01-fold.

A series of standards were made up in which $[H^{\cdot}]$ bears a known relation to the constant of the indicator. This was added in the proportion of 0·2 c.c. of a 0·01 N. solution to 20 c.c. of the standard and the colour matched in a Dubosc colorimeter.

Phenolphthalein K = $1 \times 10^{-10}$.

| $[H^{\cdot}]$ = | 10 K | K | $10^{-1}$ K | $10^{-2}$ K |
|---|---|---|---|---|
| $x$ per cent. calculated = | 9 | 50 | 91 | 99 |
| $x$ per cent. found = | 9·1 and 9·2 | 50 | 79 and 73 | 84 and 80 |

The want of agreement of the measurements in the alkaline solutions is no doubt due to the fact that phenolphthalein no longer behaves as a monobasic acid (see p. 116).

In practice colorimetric measurements were generally found to be difficult when $[H^{\cdot}]$ is less than K.

Para-nitro-phenol K = $1 \times 10^{-7}$

| $[H^{\cdot}] = 10^2$ K | 10 K | K | $10^{-1}$ K | $10^{-2}$ K |
|---|---|---|---|---|
| $x$ calculated = 1 | 9 | 50 | 91 | 99 |
| $x$ found = 1 | 6·3 and 7·3 | 50 | 100 | 100 |

*The Titration Exponent and the best Concentration of Indicator.*

The intensity of the colour is obviously proportional to the total concentration $c$ of the indicator as well as to the degree of transformation. Thus from the equation—

$$[H^{\cdot}] = K\frac{c(1-x)}{x}$$

it is clear that the absolute colour corresponding to a given $[H^{\cdot}]$ is only defined when $c$ the concentration of indicator is also defined.

Let the coloured form, whether this is $xc$ or $(1-x)\,c$, be denoted by In.

Then in the first case (coloured ion)

$$[H^{\cdot}] = K\frac{c-[In]}{[In]} \quad . \quad . \quad . \quad (1)$$

and in the second case

$$[H^{\cdot}] = K\frac{[In]}{c-[In]} \quad . \quad . \quad . \quad (2)$$

By taking logarithms and differentiating, Noyes has arrived at an expression for the optimum colour. Thus from equation (1) it may be proved that

$$\frac{d[In]}{[In]} = \frac{-d[H^{\cdot}]}{[H^{\cdot}]}\frac{c-[In]}{c}.$$

The fractional alteration in colour can never exceed that of $[H^{\cdot}]$, but approaches it as $c$ becomes indefinitely great. Practically the colour change is satisfactory when $c > 4\,[In]$, *i.e.*, when at least 75 per cent. is present in the colourless form. Thus if the lowest (molar) concentration of red phenolphthalein which can be conveniently seen is $2 \times 10^{-6}$, the total concentration must be at least four times this, *i.e.*, 0·24 c.c. of a 0·1 per cent. solution must be added to 100 c.c.

In this way the optimum colour may be defined in terms of C [In] and [H·].

The negative logarithm of the value of [H·], which corresponds to the optimum colour, has been called the titration exponent $p_T$.

Its relation to the indicator exponent $p_I$ may be obtained by taking logarithms of (1) and (2), p. 171.

$$p_T = p_I - \log \frac{c - [In]}{In} \quad . \quad . \quad . \quad (3)$$

$$p_T = p_I + \log \frac{c - [In]}{[In]} \quad . \quad . \quad . \quad (4)$$

Since $c$ is greater than 4 [In], p. 171, then from equation (3)

$$p_I - p_T > \log 3 \quad (0{\cdot}5).$$

That is to say, $p_T$ must be 0·5 less than $p_I$ in case (1), p. 171, and 0·5 greater in case (2). Similar relations hold for an indicator base, and in general the statement of p. 169 may now be made more precise by adding that the value of $-\log [H\cdot]$ at the end point of a titration should be at least 0·5 units from $\log K = p_I$ on the side of weaker colour. Thus the titration exponent $p_T$ of phenolphthalein is best kept below $p_I - 0{\cdot}5 = 9{\cdot}2$. A higher exponent gives too deep a colour.

The lowest permissible value of $p_T$ is that corresponding to the weakest possible colour $[In] = 2 \times 10^{-6}$ derived from the highest possible concentration of the indicator. The solubility $c_s$ of phenolphthalein is about $1 \times 10^{-4}$.

Then since $c - [In] = c_s$ (saturation concentration of indicator molecule)

$$p_T = 9{\cdot}7 - \log \frac{100}{2} = 8{\cdot}0.$$

Thus by altering the concentration of the indicator it is

easy to secure a considerable range of $p_T$ suitable for different titrations, *e.g.*, with phenolphthalein the correct end-points can be found in the titration of weak acids with different constants.

The greater is $c_s$ and the smaller [In], *i.e*, the greater the solubility of the indicator and the intensity of its specific colour, the further is it possible to depart from $p_T$ on the side of weak colour. The converse also holds, and so according to Noyes the difficultly soluble and weakly coloured thymolphthalein can only be employed at one value of $-\log [H^{\cdot}] = p_T$, and has practically no range of marked colour change. The limits of $p_T$ for some common indicators are as follows (Noyes):

| Indicator. | Indicator Function as Multiple of K. | $p_T$ |
|---|---|---|
| Dimethylaminoazo benzene | $0{\cdot}1\ K = 7 \times 10^{-5}$ | 4·2 |
| Methyl orange . . | $0{\cdot}1\ K = 5 \times 10^{-5}$ | 4·3 |
| Para-nitrophenol . . | 1,000 K to 3 K<br>$9 \times 10^{-5}$ to $3 \times 10^{-7}$ | 4·0—6·5 |
| Phenolphthalein . . | 20 K to 3 K<br>$4 \times 10^{-9}$ to $6 \times 10^{-10}$ | 8·4—9·2 |

*Two-colour Indicators.*—The application of the preceding equations to the change of each coloured form separately is less useful in the case of two-colour indicators, because the eye is not capable of verifying the results by estimating the

intensities of one colour in the presence of varying intensities of the other. The method of half-way change (see p. 148) is, however, particularly applicable to the determination of the constant of two-colour indicators.

The most useful range of $p_T$ may be deduced on general grounds. The colour change will clearly be unfavourable when very little of the indicator is in form (1) or in form (2). For although according to the equations already stated the relative change is great of that form which is present at low concentrations, yet the absolute change is only small and is altogether masked by the nearly constant, and stronger, colour of the other form. According to Noyes the changes from 5 to 20 per cent. or from 80 to 95 per cent. of form (1) are the best. If the two colours are of different intensity, as in the case of methyl orange and methyl red (and not merely of different tint), the change-interval is not symmetrical, and it is found, *e.g.*, in these cases, that while suitable colour changes take place with 5 to 20 per cent. in the red form, the best interval on the other side is from 20 to 30 per cent. in the yellow form. According to Bjerrum the whole interval from 15 to 85 per cent. is equally suitable in the case of a symmetrical indicator, or from 10 to 75 per cent. of red in the case of methyl orange. Comparison solutions should be used to standardise the titration exponents $p_T$. The limits of $p_T$ which should be used may now be found by introducing these results into equations (3) and (4), p. 172, which may be used on either side of the exponent of half-way change $p_I$. Thus for the change of methyl orange from red to yellow on the alkaline side, if the amount of yellow must be at least 10 per cent. of the whole,

$$p_T = p_I - \log \frac{10}{90}$$

when $p_T$ has the maximum permissible value.

Or introducing a value of $p_T$.

$$p_T < 3{\cdot}3 + \log 9 = 4{\cdot}3.$$

So also from equation (4) and on the acid side of $p_I$.

$$p_T > 3{\cdot}3 + \log \frac{25}{75} = 2{\cdot}8.$$

*Comparison between One- and Two-colour Indicators.*—With these values of $p_T$, etc., the useful range of $p_T$ for methyl orange lies between 2·8 and 4·3. The range of $p_T$ in the case of a symmetrical two-colour indicator cannot be increased by a change of indicator concentration as in the case of a one-colour. As the symmetry decreases, however, change of concentration will begin to have some effect. The ideal and typical two-colour indicator may be regarded as having a naturally wide range of $p_T$, which is independent of the concentration. This independence is particularly marked at the half-way change when $p_T = p_I$. It seems that at this point, if the colours are quite different to the eye, observers are struck mainly by the change of tint, *i.e.*, change of the ratio $\frac{x}{1-x}$, which is equal to 1 independently of the concentration, rather than by change of intensity, which depends on the concentration. This property makes two-colour indicators particularly suitable for rapid "sorting" tests in which the number of drops of indicator and the volume of solution are not taken strictly into account. Since the memory for a change of tint is good when the operator has an accurate colour sense, the advantage is secured that the $p_T$ actually used for any titration is automatically close to $p_I$. The advantage of being able to choose from the whole possible range of $p_T$ in order to secure a stoichiometrically accurate end-point in any given case is certainly lost. But, as shown in Chap. VI., corrections can always be introduced for the

deviation of $p_I$ from the hydrogen exponent of the desired end-point. If a one-colour indicator is used in the rapid manner mentioned above, there is a danger of a considerable variation in the results recorded for one and the same titration, on account of the variation in the exponent of the chosen end-point $p_T$, according to the concentration of indicator and the intensity of colour which each analyst has come to regard as correct. It appears, then, that in a laboratory where a great variety of titrations is undertaken and a good choice of indicators is available (so that $p_I$ can always be obtained close to the desired $p_T$·), the two-colour indicators are on the whole to be preferred. They seem also for these reasons to be better adapted for the match method of finding [H·] within a power of 10 (Chap. V.).

On the other hand, when a great number of titrations of exactly the same kind are performed in a fixed routine and with the highest accuracy, the balance of preference would seem to be slightly in favour of the one-colour. For the best concentrations of indicator, etc., can be found as above and colour standards can be established so that all the uncertainties inherent in the one-colour type are abolished. Certainly with these precautions equally good results may be obtained with the two-colour, but the one-colour have the advantage of not requiring a colour sense on the part of the operator and of being on the whole better adapted for quantitative colorimetry.

*The Effect of Alcohol on Indicator Colours.*—The addition of ethyl alcohol (methyl alcohol and acetone behave similarly) to a solution containing an indicator generally lessens the sensibility, *i.e.*, the indicator requires a higher value of [H·] or [OH′] in order to bring about the change. As has been stated in the sections on effect of temperature and neutral salts, the apparent sensibility to varying conditions depends upon several factors :

(*a*) The effect of these conditions upon the equilibria of other electrolytes present.

(*b*) The variation in the hydrolysis of the indicator salt itself.

(*c*) The effect on the tautomeric equilibria. That these may be greatly altered by change of solvent has been sufficiently exemplified in Chap. III.

But compounds which are useful as indicators are not so sensitive to solvents, indeed the colours and absorption spectra of many pure indicators are substantially the same in aqueous and alcoholic solution. Indicators of the amino azo group (see Chap. III., pp. 117 to 126) appear to be more sensitive to solvents.

The effect of alcohol upon salts is more marked, probably because it influences the hydrolytic equilibria. There are, however, so many equilibria which may be influenced by the alcohol that it is impossible to foretell the net effect.

Meyer and Spengler, *Ber.* 36, 2951 (1903), added alcohol to a solution of the sodium salt of phenolphthalein. The colour was discharged. This reaction was also investigated by Hildebrand, *Zeitsch. Elektrochem.*, 14, 352 (1908), and McCoy *Amer. Chem. J.*, 31, 508 (1904). It was remarked by McCoy that as little as 0·4 c.c. of alcohol makes a considerable difference to the colour of weakly alkaline solutions. These changes are in the direction to be expected if the alcohol reduces the dissociation constants of the indicators and thereby increases hydrolysis. On the other hand the addition of alcohol to methyl orange changes the colour towards yellow, while congo is changed towards red. The constants of these indicators, considered as acids, appear then to be increased.

In these experiments the problem is in its simplest terms, since no other electrolytes are present.

Other experiments, such as those of Waddell, *Chem. News*, 77, 131 (1898), require for their interpretation a

knowledge of the effect of alcohol upon the equilibria of these other electrolytes. It was found that the colours of fluorescein, cyanine, paranitrophenol, phenolphthalein, methyl orange, corallin, phenacetolin, lacmoid, and curcumin when treated with excess of strong acids and alkalies, were scarcely affected by alcohol. The present evidence seems to show that the [H·] or [OH′] of such electrolytes is scarcely affected by alcohol, but is if anything diminished. Thus Lapworth, *J. Chem. Soc.*, 107 and 108, 860 (1915), estimates the degree of dissociation of 0·1 HCl in alcohol as not more than 0·5, whereas in water it is 0·8 to 0·9. The anomalies in the transport number of [H·] and the single potential of the hydrogen electrode in alcohol (Newberry, reference in Lapworth, *loc. cit.* above) place peculiar difficulties in the way of the investigation of [H·] in aqueous alcoholic mixtures. If it is assumed, however, that with moderate additions of alcohol the [H·] values are not far from those in water, it may be stated that alcohol has little effect upon the indicator as such. It was found also by B. de Szyszkowsky that the ratio of the concentration of HCl in water to that in 1·0 N. aqueous alcohol to give the same methyl orange colour is only 0·83.

A greater effect is produced, however, when alcohol is added to indicator solutions which have been given a moderate [H·] or [OH′] by means of weak electrolytes. In accordance with the above evidence derived from strong acids and bases it may be supposed that here also it is not the indicator constant which is changed so much as that of the weak acid or base. In some of the experiments of Waddell it was found that methyl orange made red with acetic acid became yellow on the addition of alcohol, and this is probably due to a decrease in the [H·] of the acetic acid. So also the colourless acetic acid solution of cyanin is changed to blue by alcohol, the blue solution of congo to

red. Phenolphthalein reddened with ammonia becomes colourless on the addition of alcohol and acetone, while *a* naphthol benzoin changes from green to brown. Thus in each of these cases the hydrion or hydroxylion concentration as judged by colour has been reduced so that the solution becomes more nearly neutral, quite irrespective of the acidic or basic character of the indicator itself. It has been noticed by Glaser that indicators of his second group, which correspond roughly to those with $p_I$ quite near to 7, *e.g.*, lacmoid and rosolic acid, are scarcely affected by addition of alcohol. These facts also agree with the explanation just given. For if the low value of [H·] or [OH′] is produced by a low concentration of weak acid or base it cannot be much reduced by a change in the constant of the latter. If, on the other hand, it is produced by a hydrion regulator such as phosphate, then it has, according to the properties of this regulator (see Chap. V.) a steady value and one not easily changed by any change of conditions. The change in the dissociation constant of weak electrolytes due to alcohol may be supported by the evidence of conductivity, etc. It is known, *e.g.*, that the constants of salicylic and bromacetic acids are considerably depressed in alcohol, having in the pure solvent constants only $\frac{1}{10000}$ of those in pure water.

The obvious precaution to be taken in making titrations in the presence of alcohol is to perform a blank experiment or to standardise the solutions in the same concentration of alcohol. Evidently also it is undesirable in colorimetric matching experiments to use too dilute an alcoholic solution of the indicator. Precautions would appear to be particularly necessary when a colour match is being made far from the neutral point, and in solutions containing considerable amounts of weak electrolytes, since these are particularly sensitive to alcohol (see above).

# CHAPTER V

## SOLUTIONS OF STANDARD ACIDITY AND ALKALINITY

The possible range of acidity and alkalinity. The control of [H·] near the neutral point. The meaning of balanced hydrion concentration. The preparation of standards of acidity. Pure water and alkali free from carbonate. The hydrion concentration of strong acids and bases and of weak acids and bases at various concentrations. Partly neutralised weak acids and bases. The preparation and standardisation of acetate mixtures. Tables. Effect of dilution on acetate standards. Tartrate, lactate, ammonium, glycocoll, citrate, cacodylate, borate, and phosphate standards; their preparation and tables of [H·]. The application of standards and indicators to the determination of [H·]. The use of indicators alone and graphical method. Rapid colorimetric method with standards. Permanent colour standards. The treatment of coloured and turbid solutions. The effect of proteins. The effect of neutral salts. The calculation of the change in indicator exponent due to decreased ionisation. Effect of neutral salts on the [H·] of electrolytes generally. Applications. The detection of strong acids in the presence of weak acids. The alkalinity of sea water.

The methods described in Chap. I. have made it possible to prepare a number of solutions of known [H·] and [OH′]. In practice the most convenient ways of determining these are (1) by the conductivity of an acid or base; (2) by a direct measurement with the hydrogen electrode; (3) by calculation from the hydrolysis of a partly neutralised solution of a weak acid or base.

The greatest range of [H·] that can be realised experimentally is from an acid about double normal with respect to H· to an alkaline double normal with respect to OH′. These are the calculated values in solutions of 6·034 N. HCl and 6·744 N. KOH respectively. By the dilution of the

strong acids and alkalies intermediate steps are prepared which are conveniently chosen so that [H·] decreases by a power of 10 at each step of dilution. The acid, etc., concentrations are so chosen that the exponent of [H·] is a whole number. Thus by taking into account incomplete dissociation, 0·103 N. HCl is chosen in order to give 0·1 N. H·. The values of [H·] in the more dilute solutions (from 0·01 N.) are known with greater certainty than those in the strong acids for several reasons. In the latter case the interpretation of the conductivity data is more doubtful and the hydrogen electrode does not assume a steady potential. The intermediate range, however, from $[H\cdot] = 1 \times 10^{-3}$ to $[H\cdot] = 1 \times 10^{-12}$, is subject to uncertainties of another kind.

A solution 0·0001 N. with respect to HCl which should give $[H\cdot] = 1 \times 10^{-5}$ is exceedingly sensitive to traces of alkali from the glass, ammonia from the air, etc., and hence is difficult to keep and use. A similar solution of dilute alkali is, of course, rapidly affected by traces of carbon dioxide. The equilibrium of acid or alkali present in such low concentrations may also be affected by the added indicator, since in being changed the latter uses up H· and OH′, which may be comparable in amount to the electrolyte. A solution is required, then, which shall possess a low value of [H·] kept constant in the presence of acids and bases by the dissociation of a large reserve of electrolyte. The desired property is found in solutions of weak acids or bases which have been partly neutralised, for example, acetic acid and sodium acetate, ammonia and ammonium chloride. The hydrion concentrations of these may be calculated as on p. 191 with the aid of simplifying assumptions, and the results checked with the hydrogen electrode.

While partly neutralised acetic acid and ammonia afford suitable standard solutions of moderate acidity and alkalinity, they do not quite meet the need for standards

very near the neutral point, since at these values of [H·] and [OH′] the neutralisation curve (diagram, Chap. VI., p. 226) is too steep.

It is desirable, then, to use acids which have still smaller dissociation constants. The second dissociation of phosphoric acid and the first of boric acid are suitable. The steadiness of the [H·] in mixtures of $Na_2HPO_4$ and $NaH_2PO_4$ early attracted attention. Friedenthal, who prepared a whole series of steps of standard [H·], acknowledges his indebtedness to von Szily for the suggestion that the phosphates could be used to prepare those near the neutral point (*Zeitsch. Elektrochem.*, 10, 113 (1904)). Thus a mixture of $Na_2HPO_4$ and $NaH_2PO_4$ in certain proportions has the smallest possible [H·] and [OH′] ($1 \times 10^{-7}$). Yet the phosphates may themselves be present in decinormal or higher concentration. Such solutions possess what may be called a balanced neutrality, the [H·] being only slightly affected by traces of acid and alkali. They have also been called "puffer mischung," the large quantity of electrolyte acting as a "buffer" to small additions of H· and OH′.

The quantitative expression of this effect is obtained from the equations of equilibrium. Suppose that the solution of balanced acidity consists of acetic acid half neutralised with sodium hydroxide. If the total concentration of acetic acid and acetate is 0·1 N., then

$$[H\cdot] = K = 1{\cdot}8 \times 10^{-5} \text{ and}$$
$$[HA] = 0{\cdot}05,\ [A'] = 0{\cdot}05.$$

Now add so much HCl as would make the solution 0·0001 N. with respect to [H·] if no balancing solute were present.

$$[H\cdot] = \frac{(0{\cdot}05 + 0{\cdot}001)}{(0{\cdot}05 - 0{\cdot}001)} K.$$

Therefore [H·] is increased by about 4 per cent. instead of

56 times, which would have been the change if the original acidity had been produced by hydrochloric or acetic acid alone.

Again, consider the case of a mixture of primary and secondary phosphate in which all the phosphoric acid is present as $H_2PO_4$ $(1 - x)$ and $HPO_4''$ $(x)$.

Then $$[H\cdot] = K_2 \frac{[H_2PO_4']}{[HPO_4'']} = K_2 \frac{1 - x}{x}.$$

Now add "$a$" equivalents of a strong acid, the equilibrium will rearrange itself so that

$$[H\cdot]_1 = K_2 \frac{(1 - x + b)}{(x - b)}.$$

The gram ions of $HPO_4''$ "$b$" converted into $H_2PO'_4$ cannot, of course, in any case be greater than "$a$," and if this is small compared to $x$ or $1 - x$ the value of [H·] will be practically unaltered. Thus suppose that to a phosphate mixture 0·1 molar in total phosphate for which $-\log [H\cdot] = 6{\cdot}5$, HCl is added so that [HCl] total = 0·01 N. The concentration of the total alkali is reduced by this amount, and from the neutralisation curve $-\log [H\cdot]$ is reduced to 6·3. The [H·] has only been altered in the ratio $3{\cdot}16 \times 10^{-7}$ to $5 \times 10^{-7}$ by this relatively great addition of acid. Such mixtures then protect solutions against disturbances of the acidity. See also Fernbach and Hubert, *C. R.*, 131, 293 (1900); Sorensen, *Biochem. Zeitsch.*, 21, 131 (1909); Michaelis and Rona, *Biochem. Zeitsch.*, 23, 364 (1910).

In the present work these mixtures will be alluded to as mixtures of balanced [H·], or as [H·] regulators.

Any other acids or bases with suitable dissociation constants may be used as [H·] regulators. That part of the neutralisation curves (see p. 226, etc.) which is inclined at a small angle to the axis of abscissæ is suitable for the

preparation of standards, while on the other hand it is the steep part which gives a good titration.

A type of standard which is found suitable for some purposes is that in which a solid acid is present in excess. The acid (or base) must be only slightly soluble (see p. 40, Chap. I., for the general theory of such electrolytes). Fels, *Zeitsch. f. Elektrochem.*, 10, 208 (1904), who employed this method for standardising the change points of indicators, has found orthophthallic acid or para-nitro-phenol to be suitable. The former gives a flat curve from $[H^{\cdot}] = 1 \times 10^{-2}$. The acidity is easily calculated in terms of the sodium hydroxide added, since the solubility product $[H^{\cdot}]\,[A']$ is constant.

The amount of undissociated acid is equal to the solubility $C_s$ multiplied by the volume of solution; the amount of anion is equal to the amount of added NaOH, $x$. If $y$ is the volume of water added, then

$$[H^{\cdot}] = K_A \frac{C_s\,(x + y)}{x}$$

or substituting $K_A = 1{\cdot}2 \times 10^{-3}$* and $C_s = 6 \times 10^{-2}$ for orthophthallic acid

$$[H^{\cdot}] = \frac{7{\cdot}2 \times 10^{-5}\,(x + y)}{x}.$$

Now if the total volume $x + y$ is 10 c.c. the value of $[H^{\cdot}]$ is obtained from the table

| | | | | | | |
|---|---|---|---|---|---|---|
| c.c. N/NaOH = | 0 | 2 | 4 | 6 | 8 | 10 |
| c.c. water = | 10 | 8 | 6 | 4 | 2 | 0 |
| $[H^{\cdot}] \times 10^4$ = | 85 | 3·6 | 1·8 | 1·2 | 0·9 | 0·72 |

* The constant decreases slightly with rise of temperature (White and Jones, p. 189, below).

| | | | |
|---|---|---|---|
| $t$ = | 0 | 25 | 35 |
| $k \times 10^4$ = | 13·4 | 12·6 | 12·2 |

The corresponding constant $K_AC_S$ for para-nitrophenol is $7{\cdot}2 \times 10^{-9}$.

The value of heterogeneous equilibria as a basis for hydrion standards is somewhat impaired by the phenomena of supersaturation, ageing of precipitates, etc. The solubilities also often alter more rapidly with change of temperature than do the dissociation constants of electrolytes in solution.

*The Preparation of the Standards.*—In most cases it is desirable and in some cases necessary to make up the solutions mentioned below with pure water and alkali free from carbonate. The quickest and most comprehensive way of testing distilled water for the presence of electrolytes is by means of the conductivity. If this is below about $5 \times 10^{-6}$ gemmhos the water may be used without further examination. But the standard of even a poor "conductivity water" is unnecessarily high for many purposes; all that is required is that it should be moderately free from acid and alkaline impurities. It should be tested for ammonia with Nessler's reagent. The neutrality of the sample should be checked with a few drops of rosolic acid or other neutral point indicator. Most distilled water has a slightly acid reaction.

This may also be observed by the following test due to Michaelis, Die [H·], p. 172. One c.c. of litmus solution (Kubel-Tiemann extract or other pure preparation) is boiled in a test-tube. It is poured out, leaving enough to wet the sides of the tube, and filled with the water. The colour must be blue-violet, not red-violet or red.

The presence of carbon dioxide may be detected by the addition of a few drops of clear baryta solution. The water may be freed from carbon dioxide by distillation from baryta, using a tin, tinned copper, or silver condensing tube. If ammonia was present a previous distillation from acid

permanganate is necessary. A water sufficiently free from carbon dioxide for many purposes may be prepared by drawing air first through a soda lime tube about 1 metre long followed by a wash-bottle containing a little water, and then through the stock of 4 or 5 litres of distilled water. Smaller quantities of water may be rapidly freed from carbon dioxide by boiling in tinned copper vessels or in beakers or flasks of Jena glass. Flasks of ordinary glass that have been long in use or have been steamed out may, according to Michaelis, be employed for this purpose.

*Alkali free from Carbonate.*—The standards which consist of partly neutralised weak acid require for their preparation pure alkaline hydroxides. This may be made in small quantities by exposing clean pieces of sodium to the action of moist air free from carbon dioxide. The sodium supported on a funnel which may be of nickel gauze, is gradually converted into NaOH by the moist air, and falls into the platinum or porcelain basin or straight into a Jena beaker. The bell-jar stands in dilute alkali, and is fitted with a guard-tube G, containing soda lime.

Or sodium amalgam is prepared by adding gradually to sodium melted under paraffin oil about three times its weight of mercury. The amalgam is washed with petroleum ether and added in small quantities to the water free from carbon dioxide.

A fairly good sample of alkali may also be made by adding 100 grams of NaOH to 125 c.c. of distilled water in a deep stoppered cylinder (Sorensen). The carbonate settles to the bottom in about two days, and the hydroxide solution, which is about 17 N., may be siphoned through a wad of glass wool directly into the flask in which it is to be diluted. The solution may be tested after dilution by adding phenolphthalein and hydrochloric acid until the colour is pale pink, and then excess of freshly boiled neutral barium chloride. The pink colour must not vanish.

*Strong Acids and Bases.*—The [H·] and [OH'] of many solutions of strong acids and alkalies has been already given in Chap. I. The molar concentrations are determined by the usual analytical methods.

The effect of incomplete dissociation is corrected in Tables I. (Salm) and II. (Michaelis).

| Normality. | [H·] at 18° | − log [H·] | [H·] at 18° | − log [H·] |
|---|---|---|---|---|
| 1·0 | 0·78 | 0·11 | 0·8 | 0·10 |
| 0·1 | $0·91 \times 10^{-1}$ | 1·04 | $0·84 \times 10^{-1}$ | 1·071 |
| 0·01 | $0·96 \times 10^{-2}$ | 2·02 | $0·95 \times 10^{-2}$ | 2·022 |
| 0·001 | $0·98 \times 10^{-3}$ | 3·01 | $0·91 \times 10^{-4}$ | 3·013 |
| 0·0001 | | | $0·98 \times 10^{-4}$ | 4·009 |
| | I. | | II. | |

The values of [H·] in more concentrated solutions may also be derived from the conductivity measurements. In the following table the hydrion concentrations corrected for viscosity are given in the third column (Lamble and Lewis, *J. Chem. Soc.*, 10, 7241 (1915)).

The last acid concentration is that which was chosen by Salm as possessing the highest possible [H·].

*More Concentrated Hydrochloric Acid.*

| C | [H·] from conductivity. | [H·] corrected for viscosity. |
|---|---|---|
| 0·5024 | 0·425 | 0·440 |
| 0·8275 | 0·666 | 0·709 |
| 1·280 | 0·953 | 1·031 |
| 1·800 | 1·237 | 1·376 |
| 2·429 | 1·490 | 1·698 |
| 6·034 | 2·00 | |

The following concentrations according to Salm give hydrion exponents which are whole numbers :—

| $C =$ | 1·35 | 0·103 | 0·0104 | 0·001 |
|---|---|---|---|---|
| $-\log[H·] =$ | 0·0 | 1·0 | 2·0 | 3·0 |

*Alkalies.*—Sodium or potassium hydroxide may be used for making up solutions of lower acidity than $[H\cdot]=1\times10^{-12}$. The first table contains the $[H\cdot]$ values calculated by the conductivity (second line) and measured with the hydrogen electrode (third line) for solutions of potassium hydroxide (Salm).

| | |
|---|---|
| C (equivalents) = 6·8 | 1·38 |
| $[H\cdot]$ calculated = $5\cdot0\times10^{-15}$ | $2\cdot0\times10^{-14}$ |
| $[H\cdot]$ measured = $5\cdot1\times10^{-15}$ | $2\cdot0\times10^{-14}$ |
| C (equivalents) = 0·104 | 0·0102 |
| $[H\cdot]$ calculated = $1\cdot0\times10^{-13}$ | $1\cdot0\times10^{-12}$ |
| $[H\cdot]$ measured = $1\cdot3\times10^{-13}$ | $1\cdot2\times10^{-12}$ |

The following values are given by Michaelis, Die $[H\cdot]$, p. 23, for 18° C. :—

| | |
|---|---|
| C = 1·0 | 0·1 |
| $[H\cdot] = 0\cdot9\times10^{-14}$ | $0\cdot86\times10^{-13}$ |
| $-\log[H\cdot] = 14\cdot05$ | 13·07 |
| C = 0·01 | 0·001 |
| $[H\cdot] = 0\cdot76\times10^{-12}$ | $0\cdot74\times10^{-11}$ |
| $-\log[H\cdot] = 12\cdot12$ | 12·13 |

Weak acids and bases in varying concentrations may also under special circumstances be required as standards of $[H\cdot]$. It is evident from the neutralisation curves on pp. 226, 232, Chap. VI., that they are poor $[H\cdot]$ regulators, being sensitive to traces of alkalies (acids). Strong acids and bases are generally to be preferred for relatively high $[H\cdot]$ values, and some of the mixtures to be mentioned for low $[H\cdot]$ values.

When required the $[H\cdot]$ values of, say, acetic acid, can be calculated by the formulæ of Chap. I., p. 11. The values should be proportional to the logarithms of the concentrations, and this has been found to be the case by Walpole.

The hydrion concentrations of acetic acid and ammonia may be obtained from the tables:—

*Acetic Acid.*

| | | | | |
|---|---|---|---|---|
| C = | 1·0 | 0·1 | 0·01 | 0·001 |
| $[H^{\cdot}]$ = | $4{\cdot}3\times10^{-3}$ | $1{\cdot}36\times10^{-3}$ | $4{\cdot}3\times10^{-4}$ | $1{\cdot}36-10^{-4}$ |
| $-\log[H^{\cdot}]$ = | 2·366 | 2·866 | 3·366 | 3·866 |

*Ammonia.*

| | | | | |
|---|---|---|---|---|
| C = | 1·0 | 0·1 | 0·01 | 0·001 |
| $[H^{\cdot}]$ = | $1{\cdot}7\times10^{-12}$ | $5{\cdot}4\times10^{-12}$ | $1{\cdot}7\times10^{-11}$ | $5{\cdot}4\times10^{-10}$ |
| $-\log[H^{\cdot}]$ = | 11·77 | 11·27 | 10·77 | 10·27 |

The data of Chap. I. are sufficient for the construction of many more tables of this sort.

Acids which are solid, non-hygroscopic, and which can easily be obtained in a high state of purity, are particularly desirable as standards. The ionisations of some of these acids given below are taken from the results of White and Jones, *Amer. Chem. J.*, 44, 197 (1910).

The ionisation constants at different temperatures have been already given (Chap. I., p. 57).

The molar conductivities on which the ionisations are based have not been reproduced from the original paper. If required they may of course be obtained from the values of $\alpha$ and of $\Lambda$ at the given temperature.

*Succinic Acid*, per cent. ionised.

| | $t$ = | 0°. | 5·7° | 25° | 35° |
|---|---|---|---|---|---|
| V = | 8 | 2·05 | 2·15 | 2·26 | 2·28 |
| | 32 | 4·13 | 4·29 | 4·51 | 4·53 |
| | 128 | 8·18 | 8·54 | 8·80 | 8·84 |
| | 512 | 15·58 | 16·24 | 16·72 | 16·76 |
| | 1,024 | 20·47 | 22·37 | 22·91 | 22·91 |
| | 2,048 | 28·97 | 30·11 | 30·88 | 30·81 |

*Benzoic Acid*, per cent. ionised.

| | $t =$ | 0° | 15·8° | 25° | 35° |
|---|---|---|---|---|---|
| V = | 64 | 6·04 | 6·32 | 6·35 | 6·34 |
| | 128 | 8·46 | 8·92 | 8·94 | 8·92 |
| | 512 | 16·21 | 17·00 | 17·02 | 16·94 |
| | 1,024 | 21·45 | 22·62 | 22·67 | 22·52 |
| | 2,048 | 29·25 | 30·24 | 30·20 | 29·92 |

Values of limiting molecular conductivity.

| | | | | |
|---|---|---|---|---|
| $\Lambda_0 =$ | 222 | 304 | 351 | 400 |

*Salicylic Acid*, per cent. ionised.

| | $t =$ | 0° | 6·9° | 25° | 35° |
|---|---|---|---|---|---|
| V = | 64 | — | — | 22·80 | 23·02 |
| | 128 | 28·09 | 29·06 | 30·68 | 31·03 |
| | 512 | 47·28 | 48·62 | 51·34 | 51·37 |
| | 1,024 | 58·60 | 60·34 | 63·22 | 63·37 |
| | 2,048 | 68·96 | 70·73 | 73·62 | 73·36 |

*Salicylic Acid.*—Values of $\Lambda_0$.

| | | | | |
|---|---|---|---|---|
| $t =$ | 0° | 6·9° | 25° | 35° |
| $\Lambda_0 =$ | 223 | 260 | 353 | 403 |

*Hydrion Regulators derived from Weak Acids or Bases.*—The true [H·] regulators are, as already mentioned, obtained by adding to the acid or base sufficient alkali or strong acid to produce a hydrolysed mixture relatively insensitive to further additions.

The following standards are easy to prepare, have stood the test of experience, and in many cases have been checked by the hydrogen electrode. It is always desirable to repeat this check when laboratory conditions permit, although the analytical controls mentioned are also a fairly satisfactory guarantee that the solution will have the desired [H·].

*Acetate Solutions.*—Mixtures of sodium acetate with acetic acid in various proportions are a satisfactory standard between about 3·5 and 5·5.

The value of [H·] at all ordinary temperatures may be calculated with a fair degree of accuracy from the equation

$$[H\cdot] = 1{\cdot}8 \times 10^{-5} \frac{[CH_3COOH]}{[CH_3COONa]}.$$

The [H·] of this as of other good [H·] regulators is not greatly affected by moderate changes of total concentration. The equations of Chap. VI., pp. 227, 229, 239, may be used to correct for the incomplete ionisation of the salt. Accurate values of the potential of the hydrogen electrode in various acetate mixtures, against the decinormal calomel electrode have also been determined by Walpole, *J. Chem. Soc.*, 105, 2501 and 2521 (1914). From these (pp. 194, 195) the [H·] may be calculated according to p. 53, Chap. I. The solutions may be prepared from pure acetic acid which has been standardised with baryta and pure sodium hydroxide. Or sodium acetate may be taken as a standard. It is recrystallised, and since its hydrogen potential fluctuates considerably, it is standardised electrometrically in the following manner (Walpole, *loc. cit.*, p. 2517). A normal solution is made containing 13·4 grams of the recrystallised salt $CH_3COONa + 2H_2O$ in the litre of solution. To 20 c.c. of this are added 20 c.c. of N. HCl and the mixture is diluted to 100 c.c. The hydrogen potential of this should be exactly the same as that of a solution 0·2 N. with respect to both acetic acid and sodium chloride, *i.e.*, 0·493 volt against the decinormal KCl calomel electrode (connecting solution 4·1 N. KCl). If the potential is actually 0·48 volt, then on consulting the Table II., p. 195, or graph, it is seen that this corresponds to a ratio $[HCl]/[NaA] = \frac{20{\cdot}20}{20{\cdot}00}$.*

* These ratios may be obtained by interpolation from a graph in which the E.M.F.'s, column 6 (values between the asterisks in Table II. below), are plotted against c.c. of HCl, column 1.

Hence the normality of the sodium acetate is really 0·9901. This factor is then used in making up all mixtures of N. sodium acetate and N. acetic acid. The relation between the normalities of the two ingredients is found by titration of the acetic acid with baryta, "the strength of which is known exactly in terms of the N. HCl used to standardise electrometrically the normal solution of sodium acetate."

The values of Table I. refer to mixtures of acetic acid and sodium acetate which have been standardised in relation to one another by one of the above methods. The mixture which is 0·1 N. with respect to both acetic acid and sodium acetate is the particularly important standard of [H·] known as standard acetate (see Chap. I., p. 49).

This solution can be reproduced with great accuracy; it has a very small diffusion potential against potassium chloride solution, and the difference of E.M.F. due to a known error in the relative proportions of the ingredients or total concentration of the mixture may easily be calculated (Walpole, ref. above).

For the neutralisation curve of log [H·] against C or E against C (see p. 226) is in the neighbourhood of this point a straight line, and "the mean of the hydrogen potential measurements for C = 0·08 and C = 0·12 is within a tenth of a millivolt of the same value for C = 0·10, that is, 'standard acetate.'" It was also shown "that the change of this potential resulting from a change of concentration of standard acetate solution in the ratio $y$ is exactly $\log y/262{\cdot}1$ volts. Hence if in an attempt to prepare 'standard acetate' one solution be measured with theoretical accuracy and be of exact normal strength and the other be $x$ per cent. incorrect either in its standardisation or in its measurement, the difference of hydrogen potential in volts between the resulting sodium acetate—acetic acid mixture and that of the true 'standard acetate' will be—

$$\frac{x}{20}(0{\cdot}6148 - 0{\cdot}6046) \pm \frac{1}{262{\cdot}1} \log \left( \frac{100 + \frac{x}{2}}{100} \right).$$

The choice of algebraic sign, + or −, will depend on whether the incorrectly measured solution is the sodium acetate or the acetic acid and whether its strength is $x$ per cent. greater than or $x$ per cent. less than normal. In practice, however, the right hand part of this expression may be ignored entirely, for even when $x = 6$ its value only reaches 0·05 millivolt, and the statement made with all practical accuracy, that an error of 1 per cent. made in the standardisation of either solution or its measurement will lead to an error of 0·51 millivolt in the hydrogen potential of the resultant 'standard acetate' and the relationship between the per cent. error in standardisation or measuring one of the solutions and the resultant potential error, is one of simple proportion" (Walpole, ref. above).

Mixtures of sodium acetate and acetic acid may also be made by adding hydrochloric acid to the sodium acetate, and, of course, these differ from the last mentioned by containing an amount of NaCl equivalent to the free acetic acid present. The $-\log [H^{\cdot}]$, $c$ graph, is parallel to and lies slightly above that of the acetate mixtures without NaCl. The increased acidity is due in part to the interaction of NaCl and HA, in part to the effect of the "neutral salt" (see p. 218) on the strength of the acetic acid.

The two tables contain Walpole's results.

I. For mixtures of sodium acetate and acetic acid.

II. For mixtures of sodium acetate and hydrochloric acid.

The 3rd column of Table I. and the 6th of Table II. contain the E.M.F.'s of the combination—

$H_2Pt$ | solution | saturated KCl | 0·1 KCl HgCl | Hg.

TABLE I.

| $C(CH_3COOH)$. | $C(CH_3COONa)$. | $E_1$. | $E_2$. | $-\log[H^+]$. | $[H^+]$. |
|---|---|---|---|---|---|
| $0{\cdot}0_48$ | 0·19992 | 0·7785 | 0·8395 (calculated) | 8·72 | |
| $0{\cdot}0_35$ | 0·1995 | — | 0·7531 (calculated) | 7·20 | |
| 0·0025 | 0·1975 | 0·7140 | 0·7138 | 6·518 | $3{\cdot}03 \times 10^{-7}$ |
| 0·005 | 0·195 | 0·6963 | 0·6961 | 6·211 | $6{\cdot}15 \times 10^{-7}$ |
| 0·0075 | 0·1925 | 0·6855 | 0·6853 | 6·024 | $9{\cdot}46 \times 10^{-7}$ |
| 0·01 | 0·19 | 0·6781 | 0·6778 | 5·894 | $1{\cdot}28 \times 10^{-6}$ |
| 0·02 | 0·18 | 0·6595 | 0·6593 | 5·574 | $2{\cdot}67 \times 10^{-6}$ |
| 0·03 | 0·17 | 0·6479 | 0·6478 | 5·374 | $4{\cdot}23 \times 10^{-6}$ |
| 0·04 | 0·16 | 0·6394 | 0·6393 | 5·227 | $5{\cdot}93 \times 10^{-6}$ |
| 0·05 | 0·15 | 0·6317 | 0·6316 | 5·093 | $8{\cdot}07 \times 10^{-6}$ |
| 0·06 | 0·14 | 0·6257 | 0·6256 | 4·990 | $1{\cdot}02 \times 10^{-5}$ |
| 0·08 | 0·12 | 0·6149 | 0·6148 | 4·802 | $1{\cdot}58 \times 10^{-5}$ |
| 0·10 | 0·10 | 0·6047 | 0·6046 | 4·626 | $2{\cdot}37 \times 10^{-5}$ |
| 0·12 | 0·08 | 0·5947 | same as $E_1$. | 4·454 | $3{\cdot}52 \times 10^{-5}$ |
| 0·14 | 0·06 | 0·5841 | ,, | 4·27 | $5{\cdot}37 \times 10^{-5}$ |
| 0·16 | 0·04 | 0·5712 | ,, | 4·047 | $8{\cdot}97 \times 10^{-5}$ |
| 0·18 | 0·02 | 0·5525 | ,, | 3·723 | $1{\cdot}89 \times 10^{-4}$ |
| 0·184 | 0·015 | 0·5450 | ,, | 3·592 | $2{\cdot}56 \times 10^{-4}$ |
| 0·192 | 0·010 | 0·5348 | ,, | 3·416 | $3{\cdot}84 \times 10^{-4}$ |
| 0·190 | 0·008 | 0·5290 | ,, | 3·315 | $4{\cdot}84 \times 10^{-4}$ |
| 0·195 | 0·006 | 0·5225 | ,, | 3·202 | $6{\cdot}28 \times 10^{-4}$ |
| 0·195 | 0·005 | 0·5193 | ,, | 3·147 | $7{\cdot}13 \times 10^{-4}$ |
| 0·196 | 0·004 | 0·5155 | ,, | 3·081 | $8{\cdot}30 \times 10^{-4}$ |
| 0·197 | 0·003 | 0·5105 | ,, | 2·994 | $1{\cdot}01 \times 10^{-3}$ |
| 0·198 | 0·002 | 0·5057 | ,, | 2·912 | $1{\cdot}23 \times 10^{-3}$ |
| 0·199 | 0·001 | 0·4995 | ,, | 2·804 | $1{\cdot}57 \times 10^{-3}$ |
| 0·200 | 0·000 | 0·4932 | 0·4931 | 2·696 | $2{\cdot}01 \times 10^{-3}$ |

If 0·0885 volt is subtracted from this series the potentials of the saturated KCl calomel electrode against the same solutions are obtained. The 4th column of Table I. and 7th column of Table II. contain the exact E.M.F.'s of the above combination when the remaining diffusion potential has been completely eliminated by the extrapolation method

of Bjerrum (see section on hydrogen electrode), and from these the values of — log [H·] are obtained according to Chap. I., p. 53.

TABLE II.

| C.c. N·HCl Added to 20 c.c. N·$CH_3COONa$ and diluted to 100. | $C(CH_3COOH)$. | $C(CH_3COONa)$. | C(NaCl). | C(HCl). | $E_1$. | $E_2$. | — log [H·] |
|---|---|---|---|---|---|---|---|
| 0·40 | 0·004 | 0·196 | 0·004 | — | 0·7017 | 0·7015 | 6·31 |
| 1·05 | 0·0105 | 0·1895 | 0·0105 | — | 0·6763 | 0·6762 | 5·87 |
| 4·00 | 0·04 | 0·16 | 0·04 | — | 0·6375 | 0·6375 | 5 20 |
| 6·00 | 0·06 | 0·14 | 0·06 | — | 0·6235 | 0·6235 | 4·95 |
| 8·00 | 0·08 | 0·12 | 0·08 | — | 0·6125 | 0·6126 | 4·76 |
| 10·00 | 0·10 | 0·10 | 0·10 | — | 0·6017 | 0·6019 | 4·58 |
| 12·00 | 0·12 | 0·08 | 0·12 | — | 0·5905 | 0·5908 | 4·39 |
| 14·00 | 0·14 | 0·06 | 0·14 | — | 0·5790 | 0·5793 | 4·19 |
| 16·00 | 0·16 | 0·04 | 0·16 | — | 0·5651 | 0·5654 | 3·95 |
| 17·00 | 0·17 | 0·03 | 0·17 | — | 0·5560 | 0·5564 | 3·79 |
| 18·00 | 0·18 | 0·02 | 0·18 | — | 0·5457 | 0·5461* | 3·61 |
| 18·80 | 0·185 | 0·015 | 0·185 | — | 0·5385 | 0·5389 | 3·49 |
| 18·90 | 0·189 | 0·001 | 0·189 | — | 0·5293 | 0·5297 | 3·33 |
| 19·00 | 0·190 | 0·010 | 0·190 | — | 0·5270 | 0·5274 | 3·29 |
| 19·40 | 0·194 | 0·006 | 0·194 | — | 0·5155 | 0·5159 | 3·09 |
| 19·50 | 0·195 | 0·005 | 0·195 | — | 0·5135 | 0·5129 | 3·04 |
| 19·90 | 0·199 | 0·001 | 0·199 | — | 0·4945 | 0·4949 | 2·72 |
| 20·00 | 0·200 | 0·000 | 0·200 | — | 0 4898 | 0·4902 | 2·64 |
| 20·39 | ,, | ,, | ,, | 0·0039 | 0·4712 | 0·4715 | 2·32 |
| 20·89 | ,, | ,, | ,, | 0·0089 | 0·4549 | 0·4550 | 2·03 |
| 21·00 | ,, | ,, | ,, | 0·0100 | 0·4525 | 0·4525 | 1·99 |
| 21·40 | ,, | ,, | ,, | 0·0140 | 0·4443 | 0·4442* | 1·85 |
| 21·90 | 0·2000 | ,, | 0·2000 | 0·0190 | 0·4375 | 0·4372 | 1·72 |
| 22·00 | ,, | ,, | ,, | 0·0200 | 0·4365 | 0·4362 | 1·71 |
| 24·00 | ,, | ,, | ,, | 0·0400 | 0·4205 | 0·4194 | 1·42 |
| 26·00 | ,, | ,, | ,, | 0·0600 | 0·4105 | 0·4090 | 1·24 |
| 28·00 | ,, | ,, | ,, | 0·0800 | 0·4025 | 0·4007 | 1·09 |
| 32·00 | ,, | ,, | ,, | 0·1200 | 0·3935 | 0·3904 | 0·91 |
| 36·00 | ,, | ,, | ,, | 0·1600 | 0·3850 | 0·3812 | 0·75 |
| 40·00 | ,, | ,, | ,, | 0·200 | 3·3795 | 0·3750 | 0·65 |

*The Effect of Dilution on* [H·] *of Acetate Mixtures.*

The hydrogen potential of all the acetate mixtures tabulated above increases with dilution, *i.e.*, the [H·] diminishes. The change of E. with dilution varies with

the amount of acetic acid present. Thus the effect of twenty-fold dilution (0·2 N. to 0·01 N.) upon the mixtures of Table II. is about 0·075 volt when there are 40 c.c. of HCl to 20 of sodium acetate. With only 20 c.c. of HCl the increase of E on dilution is still 0·070 volt, and then falls rapidly to 0·01 volt when there is 16 of HCl to 20 of sodium acetate. The potential of the mixture equivalent to standard acetate, *i.e.*, 10 c.c. of HCl to 20 of sodium acetate only increases by 0·005 volt under the same conditions. The effect of a greater range of dilution on standard acetate is given in Table III. The meaning of $E_1$ and $E_2$ is the same as above, and [H·] may be calculated from $E_2$ in the manner already described.

TABLE III.

| | | | | | |
|---|---|---|---|---|---|
| V = | 5 | 10 | 25 | 50 | 62·5 |
| $E_1$= | 0·60360 | 0·60460 | 0·60585 | 0·60683 | 0·60735 |
| $E_2$= | 0·60345 | 0·60445 | 0·60575 | 0·60678 | ,, |
| V = | 100 | 200 | 500 | 1,000 | |
| $E_1$= | 0·60798 | 0·60923 | 0·16100 | 0·61222 | |
| $E_2$= | ,, | ,, | ,, | ,, | |

It is sometimes desirable to prepare solutions which differ from one another in respect to their [H·] and [OH′] but scarcely at all in respect to the concentrations of other ions. For example, the rate of inversion of cane sugar and the speed of many enzyme reactions are distinctly influenced by other ions, which should therefore be kept constant if the effect of [H·] alone is to be studied. This may be done by making up, *e.g.*, mixtures of sodium acetate and acetic acid in the manner described by Michaelis, Die [H·], p. 183.

The solutions have a nearly constant concentration in acetyl ion. The [H·] values in the 4th row are calculated by the formula on p. 191, above. The degree of dissociation of sodium acetate is reckoned as 0·87 throughout.

TABLE IV.

| | | | | | | |
|---|---|---|---|---|---|---|
| C.c. N/10 $CH_3COONa$ | 1·0 | throughout | | | | |
| C.c. N/10 $CH_3COOH$ . | 0·1 | 0·2 | 0·4 | 0·8 | 1·6 | 3·2 |
| C.c. water . . | 8·9 | 8·8 | 8·6 | 8·2 | 7·4 | 5·8 |
| $[H\cdot]$ . . . . | $2{\cdot}1\times10^{-6}$ | $4{\cdot}3\times10^{-6}$ | $8{\cdot}6\times10^{-6}$ | $1{\cdot}7\times10^{-5}$ | $3{\cdot}5\times10^{-5}$ | $6{\cdot}9\times10^{-5}$ |
| $-\log[H\cdot]$ . . | 5·876 | 5·366 | 5·065 | 4·770 | 4·456 | 4·161 |
| $CH_3COO'$ from salt . . . | 0·0087 | and same | throughout | | | |
| $CH_3COO'$ from acid . . . | $0{\cdot}0_521$ | $0{\cdot}0_543$ | $0{\cdot}0_586$ | $0{\cdot}0_417$ | $0{\cdot}0_435$ | $0{\cdot}0_469$ |
| $CH_3COO'$ total | 0·008702 | 0·008704 | 0·008709 | 0·008717 | 0·008735 | 0·008769 |

There are many other weak acids of which the dissociation constants will be found in Chap. I., which may be used for hydrion regulators by the directions already given. The following have been recommended by Michaelis.

*Tartrates.*—A normal solution of tartaric acid is made by dissolving 15·00 grams of the crystalline acid in 100 c.c. of water.

Half normal sodium tartrate is made from this by adding 50 c.c. of the acid to 50 c.c. of N/2 NaOH, and if necessary adding one or two drops of one or the other until phenolphthalein is just decolorised.

*Lactates.*—A 10 per cent. solution of lactic acid is boiled, standardised with pure alkali and phenolphthalein and up to normal strength. Sodium lactate (half-normal) is made in the manner described for the tartrate.

Propionate solutions may be made in the same way.

The $[H\cdot]$ values are calculated in the manner already described for acetic acid. Only the first dissociation constant of tartaric acid should be used.

A corresponding series of hydrion regulators on the alkaline side may be prepared from ammonia and ammonium chloride. The neutralisation curve is suitable between 10 and 8·5. The $[H\cdot]$ may be calculated from the equation

$$[H\cdot] = \frac{K_w \times [NH_4Cl]}{K_B \times [NH_4OH]}$$

The numerical values of $K_B$ and $K_W$ at different temperatures will be found in Chap. I. The following have been calculated by Michaelis :—

TABLE V.

| | | | | |
|---|---|---|---|---|
| Ratio $\frac{[NH_4Cl]}{[NH_4OH]}$ (18°) = | $\frac{1}{32}$ | $\frac{1}{16}$ | $\frac{1}{8}$ | $\frac{1}{4}$ |
| $[H\cdot]$ = | $1\times10^{-11}$ | $2\times10^{-11}$ | $4\times10^{-11}$ | $8\times10^{-11}$ |
| Ratio $\frac{[NH_4Cl]}{[NH_4OH]}$ = | $\frac{1}{2}$ | $\frac{1}{1}$ | $\frac{2}{1}$ | |
| $[H\cdot]$ = | $1{\cdot}6\times10^{-10}$ | $3{\cdot}2\times10^{-10}$ | $6{\cdot}4\times10^{-10}$ | |
| Ratio $\frac{[NH_4Cl]}{[NH_4OH]}$ = | $\frac{4}{1}$ | $\frac{8}{1}$ | $\frac{16}{1}$ | $\frac{32}{1}$ |
| $[H\cdot]$ = | $1{\cdot}3\times10^{-9}$ | $2{\cdot}6\times10^{-9}$ | $5\times10^{-9}$ | $1\times10^{-8}$ |

These $[H\cdot]$ values cannot be directly checked by the hydrogen electrode. The theoretical temperature coefficient is rather high ; the $[H\cdot]$ increases about fourfold between 18° and 38°. The details of the preparation of the following standards, and also their $[H\cdot]$ values are due to Sorensen unless otherwise stated. The results are expressed graphically and to scale in the diagram at end of book, and directions for the use of this and the indicator card will be found at the end of this chapter.

*Glycocoll Standards.*—Glycocoll or amino-acetic acid $CH_2(\cdot NH_2)\cdot COOH$ by virtue of its amphoteric character is capable of giving a hydrion, concentration, line of low gradient on both sides of the neutral point, *i.e.*, with slight excess of either acid or alkali.

A decinormal solution is used which contains 7·505 grams of glycocoll and 5·85 of NaCl in 1 litre. The compound

as weighed out should be free from sulphate and chloride, or contain at the most a trace of chloride. A clear solution should be obtained when 2 grams are dissolved in 20 c.c. of water. The ignition of 5 grams should give at the most 5 mgms. of ash. After the distillation of 5 grams with 500 c.c. of 5 per cent. NaOH the ammonia in the distillate should not amount to more than the equivalent of 1 mgm. of nitrogen. The nitrogen as determined by the Kjeldahl method should be $18{\cdot}67 \pm 0{\cdot}1$ per cent. of the original weight. The mixtures with decinormal HCl or NaOH are made up 10 c.c. at a time in the proportions given in the Table VI.

TABLE VI.

THE GLYCOCOLL STANDARDS.

| C.c. Glycocoll 0·1 N. | C.c. 0·1 N. HCl. | $-\log[H\cdot]$. | C.c. Glycocoll | C.c. 0·1 N. NaOH. | $-\log[H\cdot]$. |
|---|---|---|---|---|---|
| 0 | 10 | 1·04 | 10 | 0 | 6·11 |
| 1 | 9 | 1·15 | 9·9 | 0·1 | 7·81 |
| 2 | 8 | 1·25 | 9·75 | 0·25 | 8·24 |
| 3 | etc. | 1·42 | 9·5 | etc. | 8·58 |
| 4 | | 1·65 | 9·0 | | 8·93 |
| 5 | | 1·93 | 8 | | 9·36 |
| 6 | | 2·28 | 7 | | 9·71 |
| 7 | | 2·61 | 6 | | 10·14 |
| 8 | | 2·92 | 5·5 | | 10·48 |
| 9 | | 3·34 | 5·1 | | 11·07 |
| 9·5 | | 3·68 | 5 | | 11·31 |
| 9·75 | | 3·99 | 4·9 | | 11·57 |
| 9·9 | | 4·41 | 4·5 | | 12·10 |
| 10 | | 6·11 | 4 | | 12·40 |
| | | | 3 | | 12·67 |
| | | | 2 | | 12·86 |
| | | | 1 | | 12·97 |
| | | | 0 | | 13·07 |

*Citrate Standards.*—One-tenth molecular disodium citrate is made by dissolving 21·008 grams of crystalline citric acid $C_6H_8O_7 \cdot H_2O$ in 200 c.c. of normal NaOH and making up to 1 litre with pure water. The citric acid should be free from $H_2SO_4$ and HCl. When dried at 70° and 20 to 30 mm. to constant weight it should lose 8·58 ± 0·1 per cent. of its weight and remain colourless. The purity is checked by titration with 0·2 N. $Ba(OH)_2$ to a decided red with phenolphthalein. If about 30 c.c. of $Ba(OH)_2$ are used, the volume of alkali required should agree with the theoretical to about ± 0·1 c.c.

TABLE VII.

THE CITRATE STANDARDS.

| C.c. Citrate 0·1 N. | C.c. 0·1 N. HCl. | $-\text{Log}[H^+]$. | C.c. Citrate 0·1 N. | C.c. 0·1 N. NaOH. | $-\text{Log}[H^+]$. |
|---|---|---|---|---|---|
| 1 | 9 | 1·17 | 10 | 0 | 4·96 |
| 2 | etc. | 1·42 | 9·5 | 0·5 | 5·02 |
| 3 | | 1·93 | 9 | etc. | 5·11 |
| 3·33 | | 2·27 | 8 | | 5·31 |
| 4 | | 2·97 | 7 | | 5·57 |
| 4·5 | | 3·36 | 6 | | 5·97 |
| 4·75 | | 3·53 | 5·5 | | 6·33 |
| 5 | | 3·69 | 5·25 | | 6·68 |
| 5·5 | | 3·95 | 5 | | 9·05 – 10·09 |
| 6 | | 4·16 | 4·5 | | 12·07 |
| 7 | | 4·45 | 4 | | 12·36 |
| 8 | | 4·65 | | | |
| 9 | | 4·83 | | | |
| 9·5 | | 4·89 | | | |
| 10 | 0 | 4·96 | | | |

In order to obtain a flat graph in the neighbourhood of the neutral point, acids with lower constants must be used.

*Cacodylate Standards.*—The use of cacodylic acid ($K = 1 \times 10^{-6}$) has been recommended by Michaelis. A 0·1 N. solution is made by dissolving 1·38 grams of the acid in 100 c.c. of water, and from this, by mixing with an equal volume of 0·1 N. sodium hydroxide, a 0·05 N. solution of sodium cacodylate is prepared.

The extreme range is from 3·86 to 6·48, and the curve resembles that of the phosphate mixtures. The solutions are not very stable, and the useful range, from about 5·0 to 7·0 may easily be obtained with other solutions.

The standardisation with the hydrogen electrode is due to G. S. Walpole, *Biochemical Journal*, VIII., 6, 635 (1914).

| C.c. 0·2 N. Cacodylic acid. | C.c. 0·2 N. Na Cacodylate. | E. | *t.* | $-\log [H^{\cdot}]$. |
|---|---|---|---|---|
| 10 | 0 | 0·5575 | 14 | 3·86 |
| 9 | 1 | 0·6375 | 18 | 5·20 |
| 7 | 3 | 0·6675 | 16 | 5·76 |
| 5 | 5 | 0·6880 | 16 | 6·11 |
| 3 | 7 | 0·7090 | 16 | 6·48 |

*Borate Standards.*—Boric acid behaves as a weak monobasic acid. The standard is prepared by dissolving 0·2 mols = 12·404 grams of boric acid, $H_3BO_3$, in 100 c.c. of N. NaOH and making up to 1 litre.

The best boric acid "for analysis" may be used directly, or it may be recrystallised and dried at 50°.

To the borate solution is added either 0·1 N. HCl or 0·1 N. NaOH to make up 10 c.c.

The results are given in Table VIII.

TABLE VIII.

THE BORATE STANDARDS.

| C.c. Borate 0·2 N. | C.c. 0·1 N. HCl. | − log [H·]. |
|---|---|---|
| 4·75 | 5·25 | 2·37 |
| 5 | etc. | 6·55 |
| 5·25 | | 7·62 |
| 5·5 | | 7·94 |
| 5·75 | | 8·14 |
| 6 | | 8·29 |
| 6·5 | | 8·51 |
| 7 | | 8·68 |
| 7·5 | | 8·80 |
| 8 | | 8·91 |
| 8·5 | | 9·01 |
| 9 | | 9·09 |
| 9·5 | | 9·17 |
| 10·0 | | 9·24 |
| | C.c. 0·1 N. NaOH. | |
| 9 | 1 | 9·36 |
| 8 | etc. | 9·50 |
| 7 | | 9·68 |
| 6 | | 9·97 |
| 5 | | 11·08 |
| 4 | | 12·38 |

*The Phosphate Standards.*—The [H·] of mixtures of one-tenth molar solutions of primary [$NaH_2PO_4$] and secondary [$Na_2HPO_4$] solutions may be obtained directly from the neutralisation formula or graph.

| | | | | | |
|---|---|---|---|---|---|
| C.c. $NaH_2PO_4$ = 10 | 8 | 6 | 4 | 2 | 0 |
| $Na_2HPO_4$ = 0 | 2 | 4 | 6 | 8 | 10 |
| − log [H·] = 4·0 | 6·0 | 6·5 | 6·75 | 7·2 | 9·0 |

The $Na_2HPO_4 \cdot 12H_2O$ may be recrystallised from the commercial salt. The purity may be controlled by igniting 3 or 4 grams in platinum. The loss should agree with that required for $Na_4P_2O_7$ within 0·5 per cent. The aqueous solution should give a decided but not too deep pink with a few drops of phenolphthalein. The primary phosphate should also be recrystallised.

The whole of the phosphate standards may conveniently be prepared from mixtures of pure sodium hydroxide and phosphoric acid as recommended by the author (*Biochem. J.*, VI., 1 (1911)).

The normal solution may be prepared from the purest syrup (density about 1·73). This should be tested to make sure that it is free from strong mineral acids, metaphosphoric acid, and sodium phosphates. The percentage of $P_2O_5$ (about 65 per cent.) in the stock acid is found by conversion of a weighed and boiled sample into $Mg_2P_2O_7$. A weighed quantity is then diluted, boiled if necessary, to get rid of the meta- and pyro-acids, and made up to normal strength on this basis.

The sodium hydroxide for the alkaline solutions must, of course, be free from carbonate.

The salts $Na_2HPO_4 \cdot 2H_2O$ and $KH_2PO_4$ have been recommended by Sorensen as reliable standards, if prepared according to his directions.

The $KH_2PO_4$ should be carefully dehydrated. About 5 grams of the preparation dried at 100°, and 20 to 30 mm. for 24 hours should lose not more than $\pm$ 0·1 per cent. The loss on careful ignition in platinum should be (13·23 $\pm$ 0·1) per cent. The salt is also tested by dissolving 0·9 gram in 100 c.c. of freshly boiled distilled water. Three quantities of 10 c.c. are measured into test-tubes and each treated with 10 drops of para benzene sulphonic acid azo $\alpha$ naphthol.

The colour must be the same as that given by 7·5 citrate and HCl. The addition of one drop of 0·1 N. HCl to one sample and 0·1 N. NaOH to the other sample must produce a decided change. The stock solution is $\frac{1}{15}$ molecular, *i.e.*, 9·078 grams to the litre.

The hydrate $Na_2HPO_4 \cdot 2H_2O$ is made by drying the crystalline salt for 24 hours at 100° and 20 to 30 mm.

The loss on ignition of about 5 grams should be (25·28 ± 0·1) per cent. The alkalinity is tested against the borate standard. The stock solution is made $\frac{1}{15}$ molecular, 11·876 grams to the litre. The [H·] values for mixtures of these solutions are given in Table IX.

TABLE IX.

THE PHOSPHATE STANDARDS.

| C.c. N/15 $Na_2HPO_4$. | C.c. N/15 $K\,H_2PO_4$. | $-\log[H\cdot]$. |
|---|---|---|
| 0 | 10 | 4·49 |
| 0·1 | 9·9 | 4·94 |
| 0·25 | etc. | 5·29 |
| 0·5 | | 5·59 |
| 1·0 | | 5·91 |
| 2 | | 6·24 |
| 3 | | 6·47 |
| 4 | | 6·64 |
| 5 | | 6·81 |
| 6 | | 6·98 |
| 7 | | 7·17 |
| 8 | | 7·38 |
| 9 | | 7·73 |
| 9·5 | | 8·04 |
| 9·75 | | 8·34 |
| 9·9 | | 8·68 |
| 10·0 | | 9·18 |

For the use of partly neutralised mixtures of acids as [H·] regulators, see *Proc. Roy. Soc.*, A. 92, p. 463, 1916.

*The Application of Standards and Indicators to the Determination of* [$H^{\cdot}$].

One of the most important applications of the knowledge of hydrion equilibria and indicators is to the rapid colorimetric determination of acidity. The problem of finding the actual hydrion concentration of, *e.g.*, a physiological fluid, a sample of vinegar, or a natural water as it stands, is not directly solved by titration; since this is so conducted as to give the total amount of acid present, while the further deduction of the [$H^{\cdot}$] requires a knowledge of the dissociation constant, etc. The use of indicators to determine [$H^{\cdot}$] directly therefore has rendered possible a great advance in the ease with which enzyme reactions, etc., are controlled.

This direct determination requires the use of a number of indicators of which the change-points have been calibrated in terms of [$H^{\cdot}$]. When once these indicators have been prepared the process is quick and simple. It has been anticipated in details by analytical chemists, but in its more complete form is due mainly to the work of physiologists—Friedenthal, Salm, Sorensen—since it was required by them in the investigation of animal and plant juices, etc.

In 1899 Lobry de Bruyn had pointed out that congo red paper could be used to show the relative strengths of phosphoric and hydrochloric acids, and of acetic and chloracetic acids.

In 1904 Friedenthal, *Zeitsch. Elektrochem.*, 10, 114 (1904), published a table of definite hydrion steps and of change-points in which the reaction of a great number of indicators was expressed to the nearest power of 10 of the [$H^{\cdot}$]. This table was further checked and improved by Salm and others, *Zeitsch. Elektrochem.*, 10, 342 (1904); 12, 99

(1906); 13, 125 (1907); *Zeitsch. phys. Chem.*, 57, 471 (1907).

The table of indicators was also published in the monograph by Thiel, "Der Stand der Indikatoren Frage," Ahrens' *Sammlung chem. u. chem.-techn. Vorträge*, XVI. (1911).

In a chart compiled by Walpole, *Biochem. J.*, VIII., 6, 630 (1914), the change intervals of some indicators are placed alongside of the [H·], C curves of the standards of [H·].

In the chart at end of book the values of $-\log$ [H·] are plotted against the number of c.c. of the less acid constituent of the [H·] standard in 10 of the mixture. The steeper parts of the curves are not included. By the application of the edge of the card of indicators to any ordinate of the chart an appropriate indicator can be found for any standard mixture.

It is often possible to estimate the [H·] of a solution with indicators alone and without the help of standard solutions. With a fairly complete series of indicators the estimation is both quick and easy. Thus a solution which gives a transition colour with congo is thereby known to have an acidity less than [H·] $= 1 \times 10^{-3}$ (blue) but greater than [H·] $= 1 \times 10^{-5}$ (scarlet), and it is therefore placed at [H·] $= 1 \times 10^{-4}$. This value may be confirmed with another indicator having the same or a slightly different change-point. If the acidity is previously quite unknown a sorting indicator, such as methyl violet or ortho-dinitrohydroquinone, may be used.

Thus suppose that the solution which is being examined gives a reddish orange when treated with the last-mentioned indicator. With this information paranitrophenol and phenolphthalein are tried. The former gives a full yellow, the latter a colourless solution. The value of [H·] there-

fore lies between $1 \times 10^{-7}$ and $1 \times 10^{-8}$. It is not possible to fix the exponent of [H·] much within one unit by this method.

In all work for which a higher accuracy is required it will be necessary either to use the hydrogen electrode directly (where applicable) or to match the unknown solutions in a colorimeter against a graduated series of standard comparison solutions. The match may be made most accurately in one of the standard types of colorimeter, but these are not in practice much used for this purpose partly because they are not always available, or where available require some time and practice, and partly because they give a higher degree of accuracy than is necessary. A set of good Nessler glasses will serve the purpose quite well, or a set of test-tubes of colourless glass and of the same diameter. These may be arranged in a numbered stand, which is constructed so as to make an angle of 35°—40° with the vertical. They should stand on a strip of white celluloid in front of a good light.

Suppose that according to p. 206 it has been found that the [H·] of a solution lies between 7 and 8. The chart of standards shows that phosphate mixtures should be used for the comparison, and from the list on p. 158, Chap. IV., neutral red or rosolic acid are suitable indicators. The 10 standards intermediate between 7 and 8 are prepared by mixing secondary with primary phosphate according to Table IX. To each of the 10 test-tubes containing these an equal number of drops of the indicator are added, and the same number to the similar test-tube containing the unknown solution. The limit of accuracy on the colorimetric side is evidently reached when two consecutive comparison tubes cannot be distinguished from one another. The accuracy of a colour comparison by eye cannot easily be brought within 0·1 in the hydrogen exponent. With a

colorimeter it is perhaps possible to obtain results agreeing to 0·01, but such an accuracy is unnecessary and is not practicable in ordinary tests of acidity or titrations.

*Permanent Colour Standards.*

Much time would be saved if it were possible to keep a permanent set of standard [H·] solutions containing indicators. This plan, is, however, not desirable for many reasons, among which is the gradual fading and other changes which indicators undergo in time. Permanent colour standards could no doubt be prepared from inorganic salts.

Thus the different intensities of the colour of phenolphthalein may be matched, according to MacBain, *J. Chem. Soc.*, I., 101, 814 (1912), by mixtures of $Co(NO_3)_2$ and $CuSO_4$. The palest solution No. 1 contained 0·5 gram of $Co(NO_3)_2$ and 0·62 gram of $CuSO_4 \cdot 5H_2O$, together with excess of $HNO_3$ in 1 litre. The stronger coloured solutions 2, 3, 4 . . . 15 contained 2, 3, 4 . . . 15 times these concentrations. A pale colour near No. 3 was recommended to match the end-point in bicarbonate titrations.

*Coloured and Turbid Solutions.*

The matching of colours is rendered more difficult by any turbidity or specific colour which may be present in the solution which is being investigated. An indicator of the same colour is naturally excluded, *e.g.*, since most physiological fluids and many technical fluids are yellow or brown; paranitrophenol or diazo indicators would not show a clear colour change. If, however, an indicator with a sufficiently distinct colour is chosen, a match may be obtained, since the natural colour may be compensated by the addition of a suitable mixture of the following dyes, which have been

chosen by Sorensen, as they show but a slight change of colour over a large range of hydrion concentration:—

| | |
|---|---|
| Bismarck brown | 0·2 gram. in 1 litre of water. |
| Helianthin II. | 0·1 gram. in 800 c.c. of 93 per cent. alcohol + 200 c.c. of water. |
| Tropaolin O | 0·2 gram. in 1 litre of water. |
| Tropaolin OO | ,, ,, ,, |
| Curcumein | 0·2 gram. in 600 c.c. of 93 per cent. alcohol + 400 c.c. of water. |
| Methyl violet | 0·02 gram. in 1 litre of water. |

Other indicators may of course be chosen from the lists according to the tint required. Thus the colour of urine may be matched by 3 drops of Bismarck brown and 1 drop of Primrose yellow to 10 c.c. The $H^{\cdot}$ match is then made in the usual way (with litmus) (Walpole, *Biochem. J.*, V., 5, 212 (1913)).

In a modification of this method (see Walpole) the colour of the solution X which is to be tested is compensated by placing over the standard solution S a tube X′, containing the same depth as X of the coloured solution to be tested. Equal amounts of the indicator, *e.g.*, litmus in the example given, are added to X and to S. The fourth Nessler glass W contains water. The four tubes are suitably contained in a box with blackened sides, and the light is reflected through the tubes from a white surface which can be rotated on a horizontal axis.

Turbidity may be compensated in the same apparatus, or by the first method if 2 c.c. of 0·1 $BaCl_2$ and 2 c.c. of 0·1 $K_2SO_4$ are added to the standard.

The effect of toluol, chloroform, etc., which may have been added as preservatives or in order to extract fats, etc., has also been investigated by Sorensen. It is not as a rule important, and according to Michaelis may be neglected

provided that there is no toluol, etc., layer present which might actually dissolve the indicator.

*Effect of Proteins and other Colloids.*

It is well known that particles of fibres, silica, charcoal, etc., will wholly or partly remove from solution many dye-stuffs. This has been described as adsorption, and may be a surface tension or electrical effect. It has much importance in connection with the theory of dyeing, but will only occasionally affect the operations described in this book. Of more importance is the effect of colloidal substances in solution. Thus the hydrolysed salts of some metals such as aluminium exert a specific action upon indicators such as alkannin.

Organic colloids such as gelatin albumen, etc., affect most indicators, but less seriously those of a relatively simple structure, such as paranitrophenol. Congo red, which itself has a great tendency to assume the colloidal state, may in the presence of other colloids yield results which are absolutely erroneous. The indicators in Sorensen's list, p. 157, Chap. IV., have been specially chosen as suitable for physiological solutions which generally contain more or less protein. The disturbance in the results is more serious in the presence of true proteins than in that of other organic colloids. Thus a solution of glue falsifies the results on the average by 0·1 in log [H·], while white of egg may make a difference of 1·0 and even more.

When regulator mixtures are used to produce any desired value of [H·] in physiological solutions, etc., as they are, *e.g.*, in investigating the coagulation of proteids, care must be taken that they have no specific reaction on the compounds already in the solution. Borate mixtures, *e.g.*, are unsuitable for solutions containing sugars, on account of the formation of complexes. The amphoteric glycocoll is

apt to give unsteady values of [H·] in the presence of many other substances.

*Effect of Salts on the Colours of Indicators.*

Since the hydrion standards are prepared with different concentrations of different salts, it is important to verify that these have no specific effect upon the colour, since it is assumed that this is a function of [H·] alone. The assumption can be tested in the numerous cases in which the same [H·] can be prepared from entirely different salts, and it was found indeed that standard solutions in such concentrations as are used have neither any "neutral salt effect" (see below), nor do they exert on the selected indicators such specific influences as, *e.g.*, that of boric acid upon turmeric.

Thus in an experiment due to Walpole (p. 206) a borate solution made according to the directions of p. 201 gave an E.M.F. against 0·1 KCl calomel of 0·863 volt $\therefore$ $-\log$ [H·] was 9·26. An ammonium chloride solution made up to give the same tint with phenolphthalein (20 c.c. 1 per cent. $NH_4Cl$ + 0·95 c.c. N. NaOH) gave an E.M.F. of 0·862 volt $\therefore$ $-\log$ [H·] was 9·21.

The addition of such salts as NaCl, $KNO_3$, etc., in high concentration to solutions coloured with indicators undoubtedly has considerable effects upon the colour. A consistent and comprehensive explanation of these would seem to be impossible at the present time. The explanations which have been proposed follow three main directions:—

(*a*) The ordinary concepts of equilibrium in solution are taken and applied as far as the knowledge of ionic concentrations permits.

(*b*) In cases where there appears to be a residual effect inexplicable by (*a*), it has been supposed that the salt actually alters the ionisation constants of the weak acids and

bases present (including indicators). The formulation of a new constant for each salt concentration (considered as a new solvent) may indeed lead to a useful summary of the facts. The chief objection to the multiplication of such constants is that by offering a sort of substitute they tend to postpone a deeper inquiry and search for more general laws.

(*c*) It has been urged that colour changes are essentially colloidal phenomena. While it is true that many indicators easily pass into the colloidal state, and that they can be salted out as a colloidal coagulum, yet these facts by no means justify the belief that salts in causing the identical colour changes which are produced by a change of [H·], act by quite another mechanism, *i.e.*, by the production of colloidal complexes.

Some of the evidence which has led to these explanations may now be stated.

(*a*) There are certainly many cases in which the observed effect of neutral salts is that which would be expected from the ionic equilibria. Thus an ammonium chloride and a sodium borate mixture are made so that the same amount of phenolphthalein produces the same colour in each. Sodium chloride is now added to each, and it is observed that the colour of the ammonium solution becomes stronger and that of the borate weaker. Hence the salt addition does not affect the indicator directly and chiefly, since if it did so the same addition would produce the same change in both cases. But it must chiefly affect the hydrolytic equilibria of the ammonium salt and the borate, for it was to be expected that a decrease in the degree of dissociation of the salts should increase the apparent strength both of the weak base and of the weak acid, *i.e.*, decrease the hydrolysis. This diminution of hydrolysis has been observed to take place in other solutions. Thus the phenolphthalein colours

of $NaHCO_3$ and $Na_2CO_3$ mixtures are more influenced by neutral salt addition than if the original alkalinity is due to alkali hydroxide (Kuster, *Zeitsch. anorg. Chem.*, 13, 144 (1897); Schmatolla, *Ber.*, 35, 3905 (1902)).

A phosphate solution which just gives a pink with phenolphthalein, also becomes colourless when KCl is added. Now a strengthening effect of the neutral salt upon the acid or basic character of the indicator will have an opposite effect upon the colour to those just described. Therefore in these cases the hydrolysis of the carbonate, etc., appears to be more affected than that of the indicator salt. Generally speaking, it may be predicted by this theory that the neutral salt will have an effect in one direction or the other upon the colour according to whether it influences chiefly the dissociation of the other weak acids (bases) or the indicator acids (bases). If the changes of hydrion concentration and of indicator colour are determined separately, the true salt effect upon the indicator alone is probably found, and in any case the results are sufficient for practical corrections, since the [H·] values given by the hydrogen electrode are usually considered to be correct.

The salt errors of strong indicators are given in Table X. The first horizontal line gives the calculated values of the hydrogen exponent, the second those determined by the hydrogen electrode, and the succeeding lines refer to the apparent colorimetric values as determined by comparison with glycocoll solutions (see p. 199). Column A refers to pure 0·01 N. HCl, B to the same made 0·1 N., and C to the same made 0·3 N. with respect to total chloride by the addition of KCl. Assuming that the H· has the same effect whether derived from glycocoll + HCl or HCl alone, the closer agreement of the colorimetric values in column B with the electrometric can be understood, since the glycocoll also is 0·1 N. with respect to chloride (NaCl). A change of

salt concentration from zero to 0·1, then, produces a change in the negative exponent (shown by the indicator) of 2·02 — A, and one from 0·1 to 0·3 changes the exponent by C — 2·02 (last column).

Table XI. contains mainly the more acid sensitive indicators. The fourth column gives the change in the negative hydrogen exponent due to the addition of 0·5 N. NaCl. These values should be subtracted from the colorimetric negative exponents found in the presence of this salt concentration.

TABLE X.

| Indicator. | Acid or Basic. | A. | B. | C. | Apparent Alteration in Exponent with Increase of Salt. |
|---|---|---|---|---|---|
| — log [H·] calculated . | — | 2·02 | 2·04 | 2·06 | — |
| „ by hydrogen electrode . | — | 2·01 | 2·01 | 2·05 | — |
| Methyl violet . . | Basic | 2·22 | 2·04 | 1·91 | Negative. |
| Mauvein . . . | „ | 2·22 | 2·04 | 1·91 | „ |
| Gentian violet . . | — | 2·22 | 2·05 | 1·89 | „ |
| Methyl green . . | — | 2·28 | 2·05 | 1·82 | „ |
| Para benzene sulphonic acid, azo-diphenyl-amine . . . | Acid | 2·00 | 2·04 | 2·02 | Very slight. |
| Metabenzene sulphonic acid azo-diphenyl-amine (metanil yellow) . . . | „ | 1·99 | 2·04 | 2·04 | „ „ |
| Benzene, azo-diphenyl-amine . . . | Basic | 2·04 | 2·04 | 2·04 | *Nil.* |
| Para toluol, azo-benzyl-aniline . . . | „ | 2·04 | 2·04 | 2·04 | „ |

(Sorensen, *Comp. Rend. des trav. du Lab. de Carlsberg*, 9, 37 (1910); *Biochem. Zeitsch.*, 24, 415 (1910)).

TABLE XI.

| Indicator. | Acid or Basic. | [H·] Regulator Used. | Change of Hydrogen Exponent in Presence of 0·5 N·NaCl. |
|---|---|---|---|
| Para benzene sulphonic acid, azo α-naphthylamine | Acid | Phosphate | − 0·10 |
| Para nitrophenol . . | ,, | ,, | + 0·15 |
| Alizarin, sulphonic acid . | ,, | ,, | + 0·26 |
| Neutral red . . . | Basic | ,, | − 0·09 |
| Rosolic acid . . . | Acid | ,, | + 0·06 |
| Para benzene sulphonic acid, azo α-naphthol . | ,, | Borate | + 0·12 |
| Phenolphthalein . . . | ,, | ,, | + 0·12 |

It may be supposed that these experiments reveal the effect of the salt upon the hydrolysis of the indicator salt alone. Thus a borate mixture (150 c.c.) with an exponent of 8·23 was made 0·5 N. with respect to NaCl, and the exponent was thereby reduced to 8·02. The phenolphthalein colour of this solution exactly matched that of one (without salt) with an exponent of 8·14. The salt error is + 0·12.

It will be noticed from the tables that the deviations are as a rule positive for acid and negative for basic indicators. This agrees qualitatively with predictions founded on the electrolytic equilibria. The ionic colour, or tautomer, is present in higher concentration in each case than should result from the actual [H·] or [OH′]. Hence the indicator has appropriated an undue amount of base (acid), *i.e.*, its acidic or basic constant has been increased. In formula (2*a*), Chap. IV., p. **133**, a factor is introduced which expresses the incomplete dissociation of the indicator salt. This

factor becomes still more important when much neutral salt is present. In the equation

$$\frac{1-x}{x} = \frac{[H^{\cdot}]a_S}{K_A}$$

the apparent dissociation constant of the indicator acid is $K_A/a_S$, which is greater than $K_A$, *i.e.*, the apparent strength of the indicator acid is increased. The same holds of indicator bases.

By taking logarithms of equations 2*a* (and 2*b*),

$$\log \frac{1-x}{x} = \log a - p_H - \log K_A,$$

it is seen that the alteration in colour at a fixed exponent $p$ corresponds to a change of $-\log a$ in the indicator exponent. The corresponding alteration for a basic indicator is $+\log a$.

The following table due to Bjerrum, "Titrierung," p. 43, gives the values of $-\log a$ for electrolytes of different normalities and concentrations. The valency of the kathion of the added salt must be taken into account if the indicator is acid, that of the anion if the indicator is basic, according to column 1. Also the valencies of the indicators themselves must be taken into consideration if the second dissociation, etc., comes into play in the range of [H·] considered.

*Normality of Salt.*

| Valency of ions. | 0·001 | 0·01 | 0·1 | 0·3 | 0·6 | 1·0 |
|---|---|---|---|---|---|---|
| 1 and 1 | 0·01 | 0·03 | 0·07 | 0·11 | 0·13 | 0·16 |
| 1 and 2 | 0·02 | 0·06 | 0·16 | 0·25 | 0·3 | 0·4 |
| 1 and 3 | 0·03 | 0·10 | 0·26 | 0·5 | | |

The use of the table may be illustrated by the examples in Table XI., p. 215.

Thus the total salt concentration 0·1 N. of a regulator mixture was changed to 0·6 by the addition of NaCl, and therefore $-\log a$ changes from 0·07 to 0·13. The difference + 0·06 was actually verified in the case of rosolic acid, but was less than that observed for phenolphthalein. If this indicator is considered as a dibasic acid (see p. 144, Chap. IV.), then the change of $-\log a$ is from 0·3 to 0·16, agreeing with + 0·12 found.

The methyl violet bases show negative errors, and these are high, as they should be according to the valency rule. It was found by Green that solutions containing, *e.g.*, crystal violet or malachite green, which have been just changed to an orange colour by the addition of HCl, revert to the original colour on dilution with water, showing therefore an increase in the hydrolysis. The addition of salt, however, brings back the orange colour, as would be expected if it decreased the hydrolysis and increased the apparent constant $\frac{K_B}{a_S}$.

Congo also changes colour towards red, the alkaline colour on the addition of neutral salt, which would be the case if it behaved electrolytically as an acid (Michaelis and Rona, *Zeitsch. Elektrochem.*, 14, 251 (1908)).

The salt action on this indicator is highly dependent on the nature of the added salt, its valency product, etc. Indeed, in the case of other indicators also it has been found that different neutral salts in the same concentration have different effects upon the colour. Thus it has been shown that among salts with univalent anion and kathion, chlorides have a greater effect than nitrates, sodium salts than potassium salts. The great power that multivalent ions have of altering the colour is no doubt responsible for the

difference in Tables X. and XI. (effect of KCl) and Table XIII., p. 223, effect of sea-water. The higher is the salt concentration and the greater the ionic product the more does it become necessary to bear in mind the tendency of indicators to become colloidal.

*Effect of Neutral Salts upon the [H·] of Strong and Weak Acids.*

The effect of salt addition upon the [H·] of acids has been largely investigated by the velocity method. The interpretation of the results requires much calculation (see Chap. I., p. 36). The specific velocity constant of the molecules of undissociated acid is from 1·5 to 2·0 times that of the H· (Snethlage, *Zeitsch. phys. Chem.*, 85, 255 (1913); Taylor, *Zeitsch. Elektrochem.*, 20, 201 (1914)).

The observed increase of velocity in the presence of neutral salts was divided by Arrhenius among several factors. A residual increase of velocity when these had been deducted was attributed to an increase in the constant of the weak acid. According to MacBain and Coleman,* however, if the latest results for the mobility of H· are used, the catalytic activity of the undissociated strong acid formed is more than sufficient to account for the increase observed. There are also, however, many cases of an apparent increase in the strength of weak acids on the addition of salts. Thus Walpole (p. 191) has found that the E.M.F. of 0·2 N. acetic acid + 0·2 N. NaCl against the calomel electrode is lower by about 2·9 millivolts than that of the acid without the salt. According to MacBain (ref. above) 1·1 to 1·6 millivolts is due to the raising of [H·] by interaction between the acetic acid and the NaCl leaving 1·8 to 1·3 millivolts, which might be

* *J. Chem. Soc.*, 105, 1523 (1914).

accounted for by an increase in the dissociation constant of the acetic acid.

The distribution ratio of benzoic and salicylic acids between benzene and salt solutions has been determined by B. de Szyszkowski, *Medd. K. Vet. Nobelinstitut.* Bd, 2, No. 41.

Simultaneous values of the distribution of single molecules of the acids between the two solvents and of the dissociation constants of the acid in the water and salt solutions were then calculated. The reasoning should be followed in the original paper. It is criticised by MacBain and Coleman (ref. above).

The conclusion arrived at by Szyszkowski was that the constants were increased by the presence of NaCl (0·25 N. and 0·5 N.) and reached a maximum value, which is about 1·5 times that in pure water. In most cases, then, K and [H·] are changed, but only in a low ratio. If the [H·] is judged by indicators, then the actual change of [H·] may be partly or wholly compensated by the neutral salt effect on the latter. It may be useful to state here the conditions under which this compensation should theoretically be brought about.

When neutral salts are present in concentrations above, roughly, 0·1 N., acid indicators should be used in the titration of weak acids and basic indicators in the titration of weak bases, since the effects upon the acid or base which is being titrated and upon the indicators will thus be in opposite directions.

The change of acidity of carbonic acid in the presence of sodium chloride is of another order, and is probably due to a more profound disturbance of the hydration equilibrium of the $CO_2$ (see section on Carbonic Acid, Chap. VII.).

*Strong Acids.*

The addition of neutral salts can, by the nature of the case, only raise the [H·] slightly, but might decrease it

considerably. As a matter of fact Sorensen has found that it has a slight effect in increasing [H·]. It has been shown by B. de Szyszkowski (*Zeitsch. phys. Chem.*, 78, 426 (1912); 84, 191 (1913)) that the addition of salts to the halogen acids sometimes increases and sometimes decreases the acidity as judged by methyl orange. The direction of the change appears to be a specific property of the salt added, and is not additively made up of a term due to each ion. The summarised values in the table give the ratio in which the concentration of HCl has to be altered in order to show the same colour in the salt solution that it does in the water. These figures might obviously be applied to correcting the end-points in the titrations of HCl and HBr. It will be noticed that the addition of the salts in increasing concentration does not produce a regular increase or decrease of red colour, but on the contrary maxima or minima are found. Thus taking the first line, the ratio HCl in salt : HCl in water reaches a minimum between 1·0 and 0·1 N. KCl. At a still lower salt concentration Kuster (p. 315) found that HCl must be made $1{\cdot}2 \times 10^{-4}$ N. in order to give the same orange colour at $6 \times 10^{-5}$ N. HCl in water. The ratio therefore rises again to 2.

As has been stated by Bjerrum, these figures must be received with a certain amount of caution, as it is difficult to prepare with certainty hydrion concentrations below $1 \times 10^{-3}$ without using a regulator mixture.

On the whole, it seems that the effect of neutral salts either upon the [H·] of acids and bases, or upon the indicators themselves, need not be taken into account in ordinary titrations or colorimetric matches (unless carbonic acid is present in moderate amount). The correction up to a normal salt concentration is of the order of 0·1 in the exponent of [H·]. It is advisable, however, to avoid high

concentrations of salts, especially those with multivalent kathions. Also polyionic indicator acids and bases are subject to a larger error in the presence of salts.

## TABLE XII.

THE EFFECT OF NEUTRAL SALTS ON THE INDICATIONS OF METHYL ORANGE.

| Salt. | Acid. | Concentration of Acid. | Concentration of Salt. | | | |
|---|---|---|---|---|---|---|
| | | | 0·1. | 0·25. | 1·0. | 2·0. |
| KCl . | HCl . | $1{\cdot}85 \times 10^{-4}$ | 0·85 | 0·64 | 0·74 | 1·52 |
| | | $7{\cdot}14 \times 10^{-4}$ | 0·83 | 0·80 | 1·03 | 2·09 |
| NaCl . | HCl . | $1{\cdot}85 \times 10^{-4}$ | 1·19 | 1·21 | 1·91 | 1·44 |
| | | $7{\cdot}14 \times 10^{-4}$ | 0·935 | 0·97 | 1·45 | 2·24 |
| KBr . | HBr . | $1{\cdot}85 \times 10^{-4}$ | 0·95 | 0·88 | 1·66 | 2·37 |
| | | $7{\cdot}14 \times 10^{-4}$ | 0·97 | 0·92 | 1·72 | 2·35 |
| NaBr . | HBr . | $1{\cdot}85 \times 10^{-4}$ | 0·78 | 0·82 | 0·66 | 0·48 |
| | | $7{\cdot}14 \times 10^{-4}$ | 0·87 | 0·90 | 1·05 | 1·18 |

*Applications of Indicator Matching. Detection of Strong Acids in the presence of Weak Acids.*

A solution which by its reaction with methyl violet or other indicator shows an $[H^{\cdot}]$ of $1 \times 10^{-2}$ or over, will probably contain a strong acid with or without a weak one. If the probable concentration of the weaker acid is known a limit of $[H^{\cdot}]$ can be stated, beyond which the acidity cannot pass without the addition of a minimum amount of strong acid. The method has been applied to a rapid detection of the sophistication of vinegar.

In a normal solution of $CH_3COOH$ $[H^{\cdot}] = 1 \times 10^{-2\cdot9}$.
In a decinormal solution of HCl $[H^{\cdot}] = 1 \times 10^{-2}$.

The addition of methyl violet or tropaolin OO will therefore allow of the detection of 1 per cent. of mineral acid under the most favourable circumstances. The effect may be increased by the addition of alcohol (Schidrowitz, *Analyst*, 28, 233 (1903)).

In the presence of alcohol, acetic acid in all concentrations gives a yellow colour with methyl orange, whereas a strong acid gives a pink in all concentrations down to about 0·005. The solution may also be tested by spotting upon methyl-orange paper—the strong acid becoming somewhat separated by diffusion. The data of Chap. I. and this chapter are sufficient for the application of this method to many other mixtures of acids and of bases.

### *The Acidity of Natural Waters.*

The hydrion regulator of hard waters and sea-water consists of alkali carbonates. The determination of the [H·] of the former can easily be carried out with the aid of the indicators and standards of this chapter (see section on carbonic acid, p. 310).

In the case of sea-water it is necessary to know the "salt error" corresponding to the saline contents of different kinds of seas. This was determined by a device of Sorensen and Palitzsch, *Biochem. Zeitsch.*, 24, 388 (1910). Water from the Atlantic Ocean containing 35·95 per cent. of total salt was acidified with 0·2 N. HCl until — log [H·] was 2·83 (by p. benzene sulphonic acid azo-benzene benzyl-aniline). Hydrogen was then passed through in order to drive out the carbon dioxide. The water (150 c.c.) was then neutralised with 4·5 c.c. of N. NaOH and treated with 7·5 c.c. of citrate mixture. The hydrogen exponent determined by the hydrogen electrode was then 5·96, and by paranitrophenol was 6·08. The salt error was therefore

+ 0·12. The same water treated with HCl borate mixture gave an electrometric exponent of 7·10, colorimetric 7·01, and therefore the salt error is + 0·09.

In this way the table of corrections was obtained.

TABLE XIII.

| Indicator. | [H·] Regulator. | Parts per 1,000 of Salts and Corresponding Errors in Hydrogen Exponent. | | | |
|---|---|---|---|---|---|
| | | 35. | 20. | 5. | 1. |
| Paranitrophenol. | Phosphate | + 0·12 | + 0·08 | — | — |
| Neutral red . | „ | − 0·10 | − 0·05 | 0 | 0 |
| α-Naphthol- | Borate | + 0·22 | + 0·17 | + 0·03 | − 0·07 |
| phthalein | Phosphate | + 0·16 | + 0·11 | − 0·04 | − 0·13 |
| Phenolphthalein. | Borate | + 0·21 | + 0·16 | + 0·05 | − 0·03 |

The use of the table is obvious; thus if a sample of seawater treated with phenolphthalein and matched against a borate standard gives an exponent of 8·43, then the real value is 8·22. An account of the methods and results of Sorensen and Palitzsch may be of interest ("Danish Oceanographical Expedition, 1912"). The authors remark that the electrometric method which might otherwise be applied is inconvenient on board ship. Nevertheless the preservation of large samples in flasks filled up to the neck is quite possible, and some of these samples might well be taken as a check.

For the colorimetric work the only standards required are borate and hydrochloric acid. The indicators are phenolphthalein (a 0·1 per cent. solution in 50 per cent. alcohol), of which 8 drops are added to 10 c.c. of water; and α-naphtholphthalein (0·2 grams in 300 c.c. of 93 per

cent. alcohol made up to 500 c.c.), of which 6 drops are added to 10 c.c. of water. The test-tubes must be uniform in diameter (21 to 22 mm.), and are etched at 10 c.c. with hydrofluoric acid. The matching is carried out as already described. Sea-water contains about 2·3 to 2·5 milli-equivalents of bicarbonate and carbonate per litre. About $\frac{1}{10}$ of the alkali is present as carbonate according to the analyses of Schloesing and Dittmar. The variation found in the values of $[H^{\cdot}]$ must be due to the loss or gain of $CO_2$ in contact with the air, submarine springs, the water of estuaries, and also on account of the growth or decay of living organisms. In the open sea the hydrogen exponent was found to vary between the limits 7·95 and 8·35. Only in an exceptional case, the depths of the Black Sea, was the acidity as high as 7·26, and this was due to $H_2S$. The exponent found almost everywhere below the surface was 8·07 to 8·09. Thus sea-water may be said to be always alkaline by virtue of its bicarbonate. In shallow water near the land and in presence of abundant life there are much greater variations, both on the acid and the alkaline side.

# CHAPTER VI

## THE COURSE OF NEUTRALISATION AND THEORY OF TITRATION

Acids and bases forming univalent ions, strong and weak. Tables of [H·] calculated at various stages of the neutralisation. Acids (bases) forming di- and multi-valent ions. Experimental curves of some dibasic acids. General equations for the neutralisation of dibasic acids. The course of a titration and the manner in which it is related to neutralisation curves and indicator exponents. Strong acids and alkalies—corrections for end-points commonly chosen. The titration of strong acids (bases) in the presence of weaker bases (acids). The titration of weak acids (bases). The titration of the stronger acids (or bases) alone in a mixture. The mathematical theory of titration and its application to the cases mentioned above. The H· and OH′ errors. The acid and base errors. The best volumes and normalities for titrations. The errors in titrating mixtures. The theory of the titration of slightly soluble acids and bases and in the presence of slightly soluble salts. Examples and applications. The use of the hydrogen electrode in titrations. Advantages and disadvantages. Description of an electrometric titration. The acidity of tanning liquors. The titration of magnesium and calcium in dolomite.

### *Acids and Bases with Univalent Ions, Monobasic Acids and Monacid Bases.*

The values of [H·] and [OH′] for the pure acids and bases and for the hydrolysed salts have already been discussed in Chap. I. These values may also be determined at each stage of the neutralisation by the methods already described, and may then be compared with the results of calculations from the dissociation constants, etc.

A knowledge of many neutralisation curves is evidently implied in the standard solutions of last chapter, and it also permits a more scientific control of titrations than was formerly possible.

### *Strong Acids and Bases.*

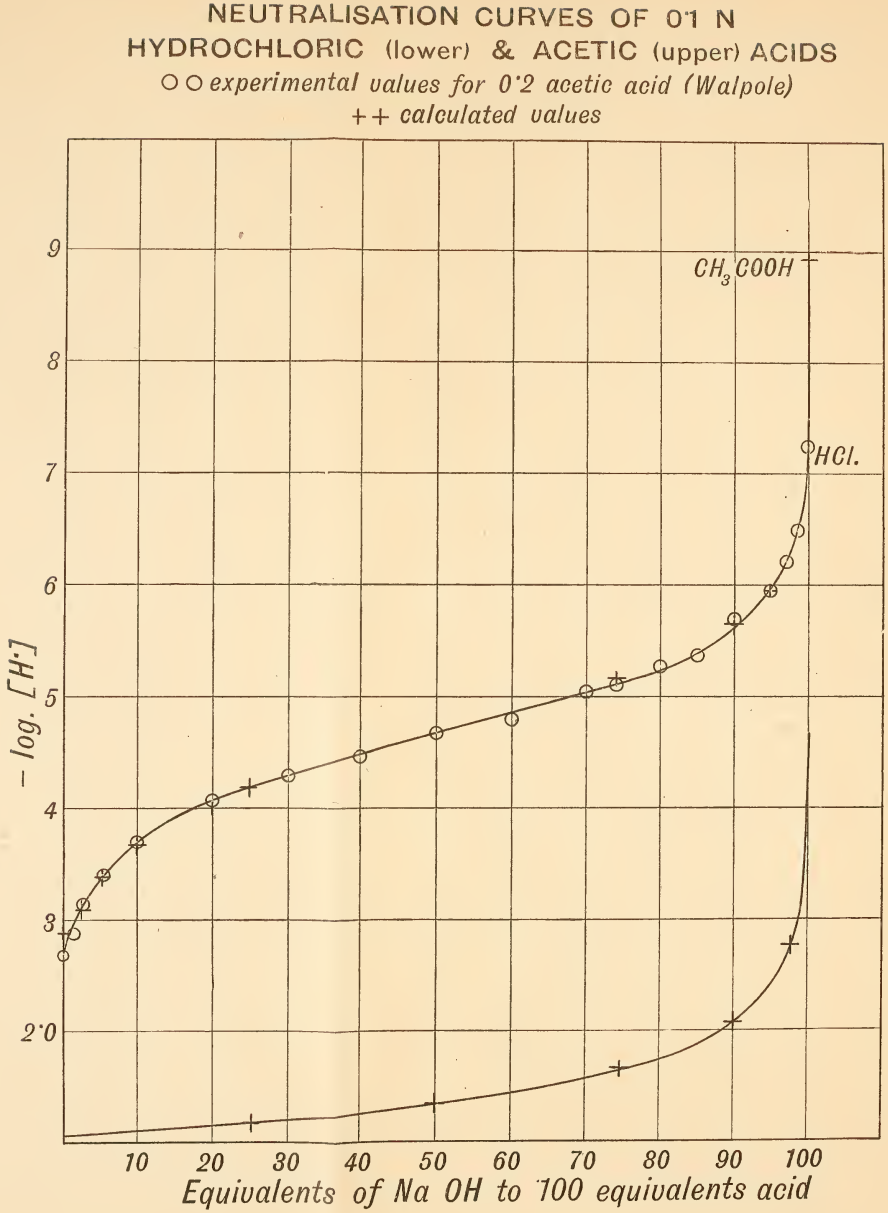
The calculations apply to a decinormal concentration of acid, base and salt. This condition can be realised experi-

mentally by adding solid alkali to decinormal acid or by adding normal alkali to 10 c.c. of normal acid and diluting to 100 c.c. The results are applicable to the usual titrations, since it can be shown that the amount of dilution which takes place during the titration has only a negligibly small effect on the hydrion concentration. The ordinates in the diagrams represent gram equivalents of strong base (strong acid) to 100 mols of acid (base) either strong or weak. The curves therefore represent the variation in $-\log [H^{\cdot}]$ with percentage of acid (base) which is neutralised.

The diagram gives the neutralisation curve of HCl by NaOH. The total chloride concentration is 0·1 N. throughout, and the degree of dissociation of the HCl has been taken as 0·9. The temperature is that at which $[H^{\cdot}] = [OH'] = 1 \times 10^{-7}$ at the neutral point (*i.e.*, about 23°).

| Alkali added, mols per cent. | Concentration of Acid left. | $-\log[H^{\cdot}]$. |
|---|---|---|
| 0·00 | 0·10 | 1·05 |
| 25·0 | 0·075 | 1·17 |
| 50·0 | 0·050 | 1·35 |
| 75·0 | 0·025 | 1·65 |
| 90·0 | 0·010 | 2·05 |
| 98·0 | 0·002 | 2·75 |
| 100·0 | 0·000 | 7·00 |

The curve of neutralisation of NaOH with HCl in which mols percentage of the latter are plotted against $-\log [OH']$ will be almost identical with diagram, but will lie a little above on account of the slightly lower degree of dissociation of a strong base at equivalent concentrations.


NEUTRALISATION CURVES OF 0·1 N
HYDROCHLORIC (lower) & ACETIC (upper) ACIDS
○ ○ experimental values for 0·2 acetic acid (Walpole)
++ calculated values
$CH_3COOH$
HCl.
9
8
7
6
5
4
3
2·0
− log. [H·]
10
20
30
40
50
60
70
80
90
100
Equivalents of Na OH to 100 equivalents acid

*Weak Acids and Bases.*

The neutralisation of acetic acid is typical of that found in the case of all those electrolytes which obey the dilution law. The experimental results of Walpole have been already given in Chap. V., and it only remains to state the formulæ which are required at each stage of the neutralisation. Let C be the concentration of total acetate, hydrogen and sodium, and $C_1$ that of sodium acetate. Then the free acetic acid $= C - C_1$ ($C_A$).

(1) When $C_1$ is small an appreciable part of the acetyl ion is derived from the free acetic acid.

$$[H\cdot] = -\frac{C_1}{2} + \sqrt{\frac{C_1^2}{4} + KC_A} \quad . \quad . \quad (1)$$

This equation holds for dilute solutions in which the dissociation of the sodium acetate is practically complete. In a 0·1 N. acetate solution the degree of dissociation may be taken as that of the sodium acetate present at any stage, or at a mean value corresponding to the half-neutralised acid (0·05 sodium acetate in this case) or as that of the total acetic acid + acetate present. The difference in the values of [H·] obtained is not great. Thus, using formula 1 for 0·1 acetic acid, which is 2 per cent. neutralised, and putting $a_s = 0{\cdot}79$, $-\log [H\cdot] = 3{\cdot}12$, while for 0·2 N. acetic acid 2 per cent. neutralised and $a_s = 0{\cdot}95$ (as in 0·0038 N. sodium acetate) $-\log [H\cdot] = 3{\cdot}11$.

The table below has been calculated with $a_s = 0{\cdot}79$ throughout. For $C_1$ is substituted $a_sC_1$ and $K = 1{\cdot}8 \times 10^{-5}$.

(2) From about 5 per cent. neutralisation onwards $aC_A$ (acetyl ion from acetic acid) becomes negligible compared to $a_sC$, and the formula becomes

$$[H\cdot] = \frac{KC_A}{a_sC_1} \quad . \quad . \quad . \quad . \quad (2)$$

(3) At the point of chemical neutrality [H·] can be calculated from the formulæ of hydrolysis (pp. 29 to 32). The degree of hydrolysis of sodium acetate is $0{\cdot}0_48$ (Walker) at $C = 0{\cdot}2$. Therefore $[H\cdot] = 4{\cdot}62 \times 10^{-10}$, $-\log [H\cdot] = 9{\cdot}34$.

If the incomplete dissociation of the salt and alkali be taken into consideration ($a_S = 0{\cdot}79$ $a_B = 0{\cdot}9$), formula (4a), p. 30, the value of [H·] becomes $1{\cdot}34 \times 10^{-9}$ (exponent 8·87). These values are difficult to obtain experimentally on account of the great fluctuation caused by the least trace of excess acid. The highest value of the E.M.F. against 0·1 KCl calomel is 0·7785, corresponding to $-\log [H\cdot] = 8{\cdot}72$.

In the rest of the curve the agreement of the calculated values with those found by Walpole at $C = 0{\cdot}2$ is good as will be seen by the comparison of the table below with Table I., p. 19, Chap. V. See diagram above.

*The Neutralisation of* 0·1 *N. Acetic Acid.*

| Equivalents per cent. of Alkali. | [H·]. | $-\log$ [H.]. |
|---|---|---|
| 0 | $1{\cdot}33\times10^{-3}$ | 2·88 |
| 2 | $7{\cdot}6\times10^{-4}$ | 3·12 |
| 5 | $4{\cdot}0\times10^{-4}$ | 3·40 |
| 10 | $2{\cdot}05\times10^{-4}$ | 3·69 |
| 20 | $9{\cdot}10\times10^{-5}$ | 4·04 |
| 25 | $6{\cdot}83\times10^{-5}$ | 4·17 |
| 50 | $2{\cdot}28\times10^{-5}$ | 4·64 |
| 75 | $7{\cdot}60\times10^{-6}$ | 5·12 |
| 90 | $2{\cdot}53\times10^{-6}$ | 5·60 |
| 95 | $1{\cdot}20\times10^{-6}$ | 5·92 |
| 100 | $1{\cdot}34\times10^{-9}$ | 8·87 |

The equations developed above will apply also to stronger acids provided that they obey the dilution law fairly closely,

*e.g.*, the constant 0·021 for formic acid holds from V = 32 to V = 1,024. Since, however, the values of [H·] at each stage of the neutralisation are much higher it is not permissible to consider the total free acid as undissociated. The complete equation must be written

$$[H\cdot]\{a_s C_1 + a(C - C_1)\} = K\{(C - C_1) - [H\cdot]\}$$

and

$$[H\cdot] = -\frac{a_s C_1 + K}{2} + \sqrt{\left(\frac{a_s C_1 + K}{2}\right)^2 + K(C - C_1)}. \quad (3)$$

A more general equation, which is deduced similarly to that of (1*a*) and (1*b*) on pp. 239, 240, contains a term which expresses the OH′ error and also the effect of changes in the total concentration.

If R is the ratio of equivalents of alkali to mols of acid, then:

$$R = \frac{1 + \frac{K_W}{[H\cdot]a_B[NaA]}}{1 + \frac{[H\cdot]a_s}{K}} \quad . \quad . \quad . \quad (4)$$

The use of this equation is illustrated on p. 278, Chap. VII. (boric acid).

The equations expressing the neutralisation of electrolytes which obey the dilution law can be much simplified in some cases (Michaelis, Die [H·], p. 18).

The degree of dissociation "*a*" of an acid or base is somewhat extended in meaning so as to include cases in which the total acid (base) is present partly as "free" acid and partly as salt (see Chap. I., p. 13). The degree of dissociation is defined as the ratio of

$$\frac{\text{Total acid anion}}{\text{Total acid in any form}} = \frac{A'}{[HA] + [BA] + [A']}.$$

This ratio has been called the "ion fraction." The dissociation residue $\rho$ is defined as the ratio

$$\frac{[HA]}{[HA] + [BA] + [A']}.$$

It has been called the "ion residue."

It is clearly only identical with $1 - \alpha$ as usually defined when [BA] or undissociated salt is a negligible quantity. When it is appreciable a suitable correction may be introduced into the simplified equation. The dissociation constant under these conventions acquires a somewhat different meaning also, since

$$K' = \frac{[H\cdot]\alpha}{\rho}$$

is not always the same as

$$K = \frac{[H\cdot]\alpha}{1 - \alpha}.$$

When K is the same as K′, then the log [H·], $\alpha$ curve, agrees with the neutralisation curve, since the amount of acid anion present at any point is equal to the added alkali. The difference caused by neglecting $\alpha_s$, etc., in equations 2 and 4 may be illustrated from the acetic acid neutralisation.

By the equation on p. 13, Chap. I., $\alpha = 0{\cdot}5$ when $[H\cdot] = K$. In the case of acetic acid, then, the ordinate from 50 on the diagram should strike the neutralisation curve at $-\log [H\cdot] = 4{\cdot}745$, whereas the value calculated by formula 2 is 4·64.

At this point the $\alpha$, $-\log [H\cdot]$, and $\rho$, $-\log [H\cdot]$, curves deduced from equations (Chap. I., p. 13) cut one another, and it is also the point at which the rate of increase of the differential $\frac{d \log [H\cdot]}{d\alpha}$ changes its sign.

This tangent of the slope of the curve has the same value

$= 1{\cdot}737$ for all electrolytes, and the angle is therefore slightly greater than 60°. The $\rho$ curve is the mirror image of the $\alpha$ curve. The $\alpha$ and $\rho$ curves are identical for all acids to which the simplified formulæ apply, but they are moved in one direction or the other along the axis of abscissæ so that the singular point falls on the ordinate numerically equal to log K. The $\alpha$, $\rho$ curves of bases are identical with those of acids if [OH′] is substituted for [H·]. If [H·] is retained the curves of bases are the mirror images of those of acids.

The $\alpha$ curves are identical with the correct neutralisation curves * only at concentrations less than those at which the dissociations of salts strong bases, etc., become appreciably less than 1 and greater than those at which the [H·] or [OH′] have a concentration which is considerable compared to those of the other ions present. These conditions are fairly well realised at concentrations of 0·01 to 0·005. At this concentration the neutralisation curves of weak (acetic) and very weak (phenol) acids, also of weak (ammonia) and very weak (parachloraniline) bases, assume the form of diagram which has been calculated (p. 321) by Thiel from the constants $1{\cdot}8 \times 10^{-5}$ and $1{\cdot}3 \times 10^{-10}$.

The curves of a strong acid and base are added for comparison.

Attention may now be called to certain properties of these curves which are important for the theory of titration.

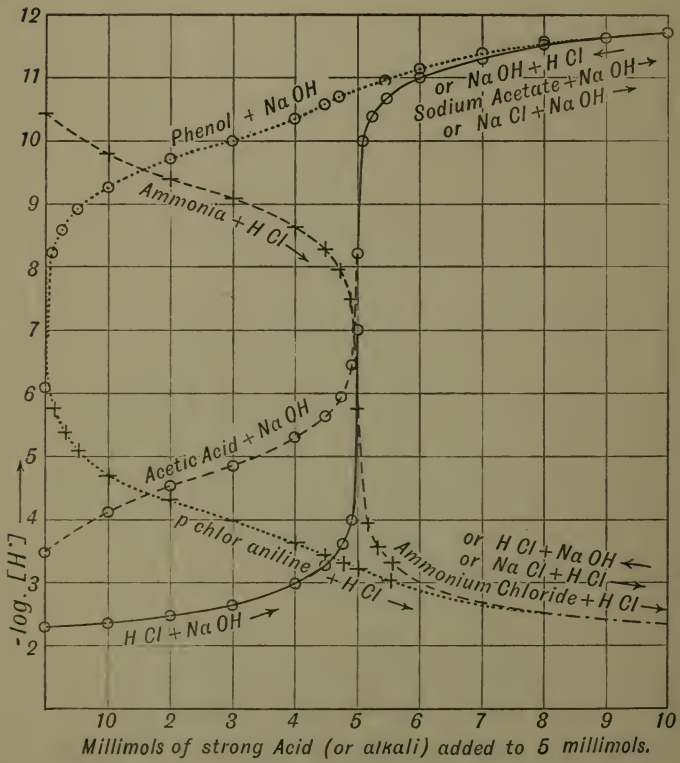
In the case of the strong acid the acid branch has a gradual slope, but after 90 per cent. has been neutralised the neutral branch has a very steep slope. Since the [H·] of the solution passes through many powers of 10 on the addition of minimal amounts of acid and alkali, the sharpest

* *I.e.*, for a weak acid or base, approximately :

Fraction neutralised = ion fraction $\alpha$
Fraction remaining = ion residue $\rho$.

titrations are possible. The point of stoichiometrical coincides with that of absolute neutrality. The succeeding alkaline branch has a gradual slope.

In the case of a weak acid and strong base the slope is




Neutralisation curves of 0·005 N. acids and bases calculated from their ionisation constants.

moderately steep at the beginning of the titration, becomes then nearly horizontal, but is steep enough again at the end-point for a good titration. The point of stoichiometrical neutrality is alkaline, and as shown by Hildebrand (*J. Amer.*

*Chem. Soc.*, 35, 847 (1913) ), is located in the middle of the perpendicular part of the curve. The alkaline branch coincides with that of a strong acid.

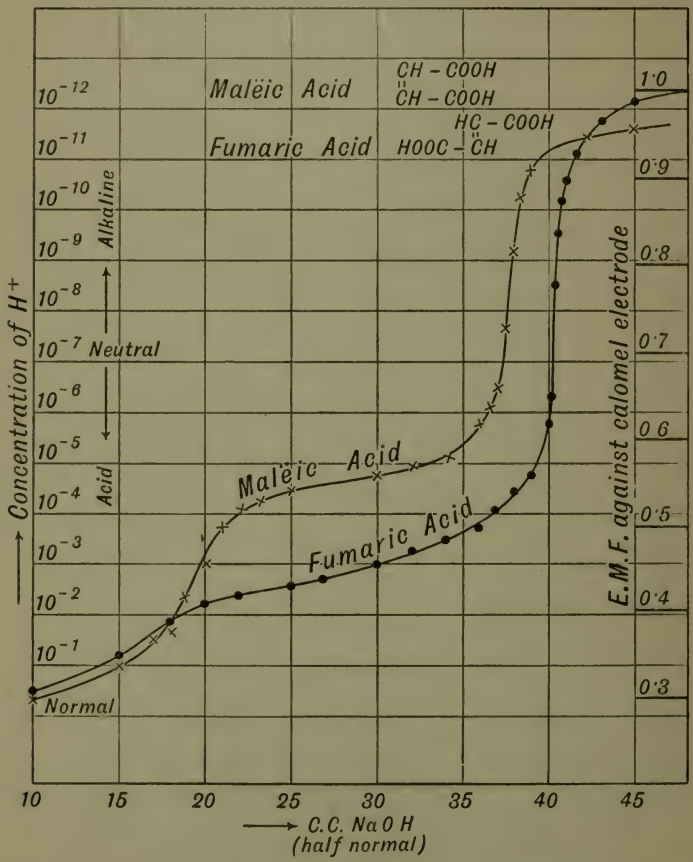
In the case of a very weak acid and strong base the slope is steep at the beginning of the titration but in no other part. It becomes very slightly steeper when an equivalent of alkali has been added. The alkaline branch does not coincide with that of a strong acid until a considerable excess of alkali has been added.

At very high dilutions the second term of the numerator in equation 4, p. 229, becomes increasingly important. A high [H·] or [OH′] is now impossible (see section on dibasic acids, p. 240, and on carbonic acid, p. 309). The neutralisation curves of all electrolytes become more nearly horizontal at high dilutions and approach towards one another and the line of absolute neutrality.

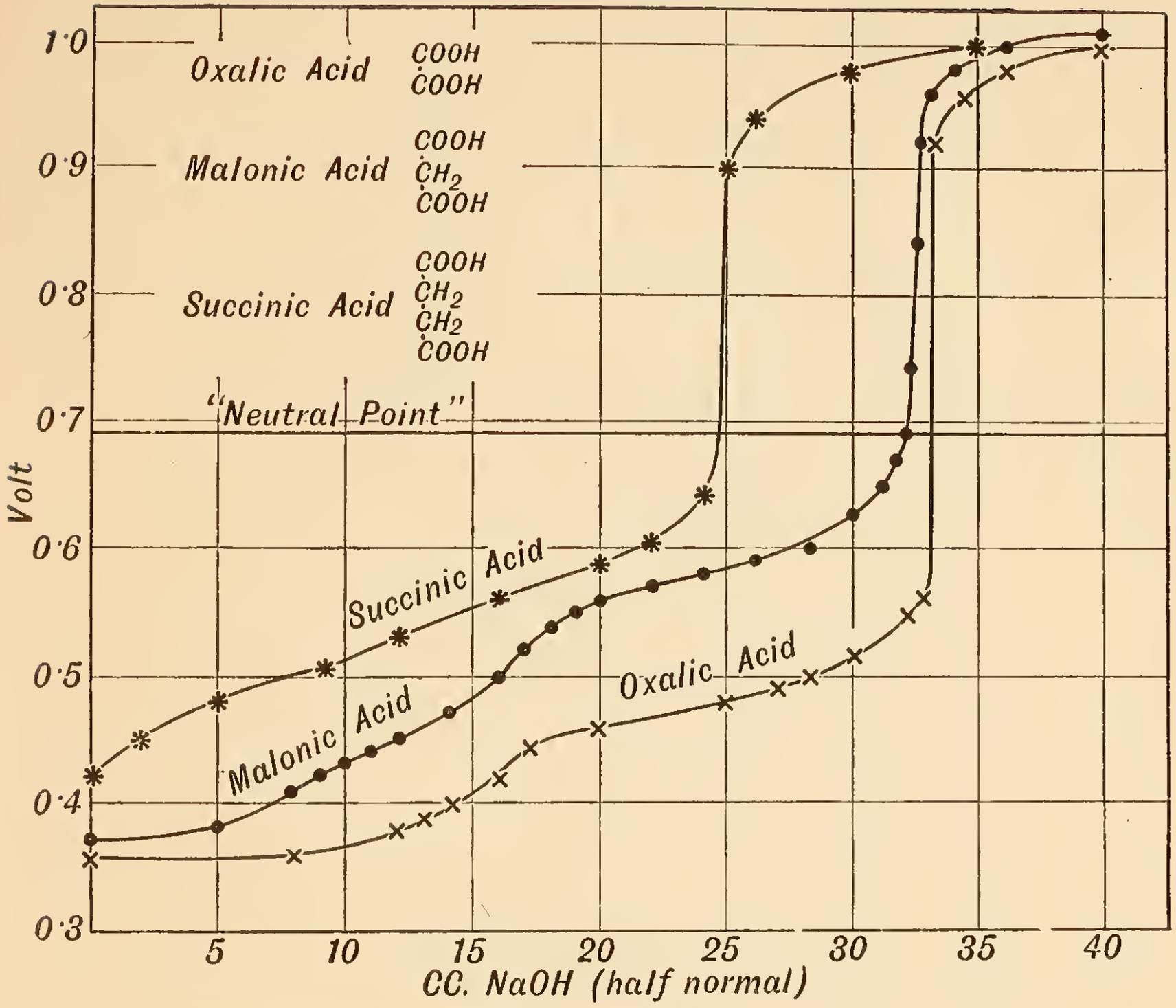
*Neutralisation of Di- and Poly-hydrion Acids.*

The curves of neutralisation of these acids often show one or more inflections corresponding to the successive stages of basicity. At these points the rate of evolution of heat, the rate of change of [H·] (and of other physical properties also) for equal increments of alkali, changes more or less sharply, and according to the number of inflexions two or more constants will be required to express the course of neutralisation. But, on the other hand, it is possible that a neutralisation which can be expressed by one constant is really governed by two or more. For the nature of the curve will correspond to the relative values of $K_1$ and $K_2$, etc. When the constants are both high, as in the case of $H_2SO_4$, the dissociation of which is almost complete at moderate concentrations, the curve is that of a monohydrion acid. The same appearance recurs when $K_2$ is so exceedingly small that the hydrolysis of the second H· is

almost complete. Examples of this are probably to be found in boric acid and in phenolic acids, such as salicylic. When $K_1$ is nearly equal to $K_2$ the inflection is very slight,




as in the curves of succinic and citric acid, but when the ratio, of $K_1$ to $K_2$ is slightly greater a more marked inflection appears as in the curve of malonic acid. The greater the ratio, the more marked is the inflection, as is easily seen by




Neutralisation Curves of Succinic, Malonic and Oxalic Acids.

a comparison of the curves of maleic and fumaric acids. The ratio $K_2/K_3$ is of the order $10^5$ in the case of phosphoric acid.

In carboxylic acids, if the presence of each COOH does not increase the constant of the other, then the combined constant of the acid dissociating in two ways is at least twice that of either COOH group separately (Chap. I., p. 20). And Walker has found that in many cases the constant of a symmetrical acid is twice that of the mono-ester acid (*J. Chem. Soc.*, 61, 69 (1892)). Thus for suberic acid $COOH(CH_2)_6COOH$, in which it may be supposed that the COOH will have relatively little influence on one another, $K_1$, for the acid is $2{\cdot}96 \times 10^{-5}$, and K for ester acid $COOH(CH_2)_6COOH$ is $1{\cdot}46 \times 10^{-5}$.

Yet even in this case the presence of the electron from the first dissociation so modifies the second constant that while $K_1$ is $3 \times 10^{-5}$, $K_2$ is $0{\cdot}25 \times 10^{-6}$. In practice the ratio of $K_1$ to $K_2$ is seldom below about 25. This only gives, however, a very slight inflection.

### *Strong Dibasic Acids.*

The neutralisation of these acids follows practically the same course as that of a monobasic acid, as will be seen by a comparison of the curve for $H_2SO_4$ (Enklaar, *Zeitsch. phys. Chem.*, 80, 620 (1912)) with that for HCl.

The abscissæ in the former case being equivalents of alkali to 1 mol of acid, the percentage neutralised is represented on twice the scale. If the abscissæ are equivalents of alkali to one equivalent of sulphuric acid, it will be seen that this curve is almost identical with, but lies slightly higher than, the curve for HCl. It will be seen, then, that the second dissociation (of $HSO'_4$) must be as great as the first.

The anion $HSO'_4$ is itself a strong acid.

In the experiments of Enklaar, of which the results are tabulated below, the solution was made from 10 c.c. of normal sulphuric acid to which were added the volumes of normal sodium hydroxide given in the first rows, the whole being then made up to 100 c.c.

| | | | | |
|---|---|---|---|---|
| C.c. N. NaOH = | 0 | 0·5 | 1·0 | 1·5 |
| $-\log[H^\cdot]$ = | 1·2322 | 1·2582 | 1·2825 | 1·3085 |
| C.c. N. NaOH = | 2·0 | 2·5 | 3·0 | 3·5 |
| $-\log[H^\cdot]$ = | 1·3414 | 1·3820 | 1·4246 | 1·4731 |
| C.c. N. NaOH = | 4·0 | 4·5 | 5·0 | 5·5 |
| $-\log[H^\cdot]$ = | 1·5182 | 1·5667 | 1·6326 | 1·6626 |
| C.c. N. NaOH = | 6·0 | 6·5 | 7·0 | 7·5 |
| $-\log[H^\cdot]$ = | 1·7261 | 1·7833 | 1·8655 | 1·9463 |
| C.c. N. NaOH = | 8·0 | 8·5 | 9·0 | 9·5 |
| $-\log[H^\cdot]$ = | 2·0589 | 2·2115 | 2·3969 | 2·7262 |
| C.c. N. NaOH = | 10·0 | 10·5 | 11·0 | |
| $-\log[H^\cdot]$ = | 7·1543 | 11·669 | 12·085 | |

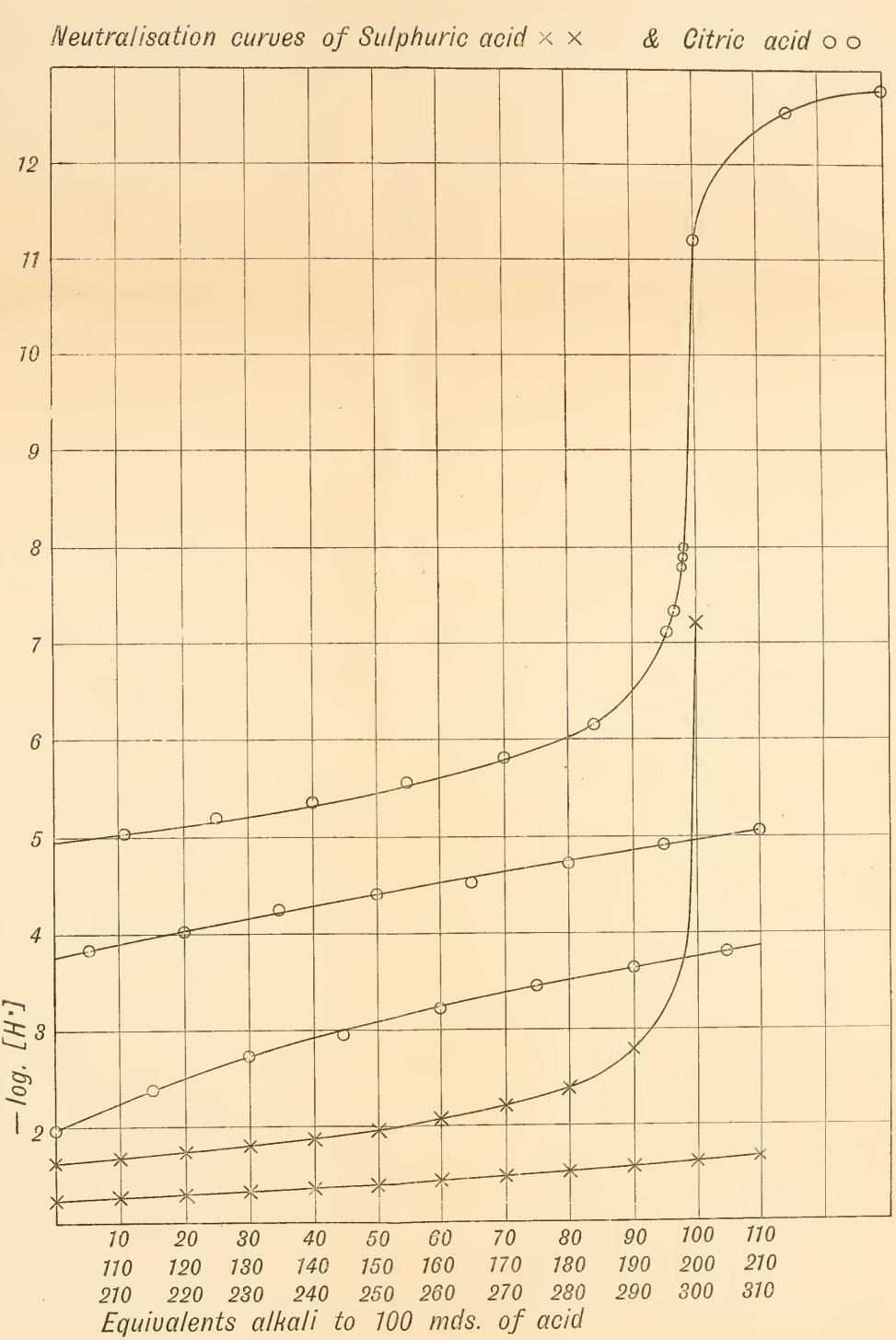
*General Equations for the Neutralisation of Dibasic Acids.*

In cases where dissociation constants $K_1$ and $K_2$ into primary HA′ and secondary A″ ions can be stated, the ion fractions $a_1$ and $a_2$ and the ion residue $\rho$ as defined in this chapter, p. 230, may be expressed as functions of $[H^\cdot]$, $K_1$ and $K_2$. It has been shown by Michaelis, Die $[H^\cdot]$, p. 30, that

$$a_1 = \frac{1}{1 + \frac{[H^\cdot]}{K_1} + \frac{K_2}{[H^\cdot]}} \quad . \quad . \quad . \quad (1)$$

$$a_2 = \frac{1}{1 + \frac{[H^\cdot]}{K_2} + \frac{[H^\cdot]^2}{K_1 K_2}} \quad (2) \qquad \rho = \frac{1}{1 + \frac{K_1}{[H^\cdot]} + \frac{K_1 K_2}{[H^\cdot]^2}} \quad (3)$$

The ion fractions $a_1$ and $a_2$ are here defined as the ratio


Neutralisation curves of Sulphuric acid × ×  & Citric acid ○ ○
12
11
10
9
8
7
6
5
4
3
2
— log. [H·]
10 20 30 40 50 60 70 80 90 100 110
110 120 130 140 150 160 170 180 190 200 210
210 220 230 240 250 260 270 280 290 300 310
Equivalents alkali to 100 mds. of acid

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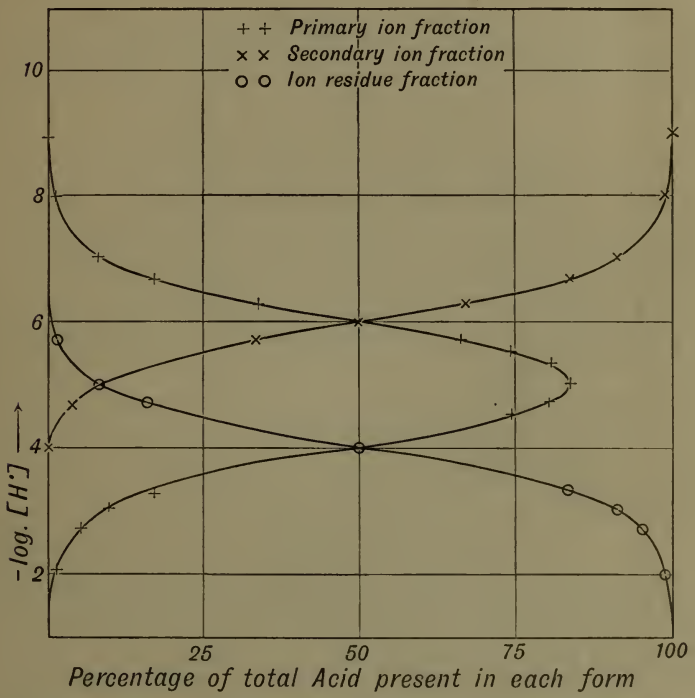
of the primary HA′ and secondary A″ ion respectively to the total acid in any form of combination. It is assumed that the primary salt dissociations are approximately equal




to 1 and that the production of H· or OH′ uses up only a negligibly small fraction of the total salt present.

The diagram shows the above functions in the cases that

$$(1)\ K_1 = 1 \times 10^{-4} \quad K_2 = 1 \times 10^{-6}$$

(1) When the first dissociation constant is much greater than the second, the first dissociation is almost complete before the second begins. The $a_1$ curve has nearly the

form of that of a monobasic acid with the same constant, and the point at which the $a_1$ curve changes direction occurs at $[H^{\cdot}] = K_1$. Here the $a_1$ curve cuts the $\rho$ curve and $a = \rho = 0{\cdot}5$.

The maximum value of $a_1$ is practically equal to 1. It is given by the equation—

$$a_1 \text{ (maximum)} = \frac{1}{1 + 2\sqrt{\frac{K_2}{K_1}}} \quad . \quad . \quad (4)$$

The $\rho$ and $a_2$ curves are well separated from one another, and there is therefore no undissociated acid present when the ions A″ begin to be formed (at the expense of HA′).

(2) As $K_1$ approaches $K_2$ in magnitude, the $a_2$ and $\rho$ curves begin to overlap. The two kinds of dissociation proceed together almost from the first. The maximum value of $a_1$ decreases according to equation (1) above and the $a_1$ curve becomes more pointed. The value of $[H^{\cdot}]$ at the maximum concentration of primary ions is given by the equation—

$$[H^{\cdot}] = \sqrt{K_1 K_2} \quad . \quad . \quad . \quad . \quad (5)$$

These equations give satisfactory results when the assumptions made in their deduction correspond, or nearly so, to the facts.

For solutions of higher or of very low concentration, however, it is necessary to deduce more general equations of the type (4), p. 229. These are obtained by a method similar to that used by the author in correcting the third dissociation constant of phosphoric acid (see p. 287). Terms are introduced which express the fraction $a$ of the salt dissociated and others which contain the total salt concentration C and the excess $[H^{\cdot}]$ or $[OH']$. In order to compare the result (6) below with the simplified form, equations (1) and (2) above have been transformed. If

the total acid concentration is C, then the ionised parts are $a_1C$, etc., and the number of equivalents of ionised acid are equal to the added base.

Hence

$$\frac{\text{Equivalents alkali}}{\text{Mols acid}} = R = \frac{A' + 2A''}{C} = a_1 + 2a_2$$

and

$$R = \frac{1}{1 + \frac{K_2}{[H\cdot]} + \frac{[H\cdot]}{K_1}} + \frac{2}{1 + \frac{[H\cdot]}{K_1} + \frac{[H\cdot]^2}{K_1K_2}}$$

In deducing the more comprehensive equation let $a_1$, $a_2$ and $a_3$ now represent the degrees of dissociation of the primary and secondary salt and of the sodium hydroxide formed by hydrolysis.*

Then

$$[NaHA] = \frac{[HA']}{a_1} \qquad [Na_2A] = \frac{[A'']}{a_2}$$

$$[NaOH] = \frac{[OH']}{a_3} = \frac{K_W}{[H\cdot]a_3}$$

And the ratio R as defined above is equal to

$$\frac{[NaHA] + 2[Na_2A] + [NaOH]}{[NaHA] + [Na_2A] + [H_2A]}$$

By substitution, these equations can be expressed in terms of (1) [NaHA], (2) [$Na_2A$], and on dividing numerator and denominator by these concentrations it follows that

$$R = \frac{1 + \frac{2K_2a_1}{[H\cdot]a_2} + \frac{K_W}{[H\cdot][NaHA]a_3}}{1 + \frac{K_2a_1}{[H\cdot]a_2} + \frac{[H\cdot]a_1}{K_1}} . \qquad (1a)$$

* Prideaux, *Proc. Roy. Soc.* 91 A, 535.

or
$$R = \frac{2 + \frac{[H\cdot]a_2}{K_2a_1} + \frac{K_w}{[H\cdot][Na_2A]a_3}}{1 + \frac{[H\cdot]a_2}{K_2a_1} + \frac{[H\cdot]^2a_2}{K_1K_2}} \quad . \quad . \quad (1b)$$

For solutions containing only small amounts of alkali (1*a*) may be employed, and (1*b*) if the neutralisation is nearly complete. For intermediate solutions containing appreciable amounts of both HA′ and A″ the two equations give identical results. These equations may be applied to all the experimental neutralisation curves quoted. For all the common acids considered, with the possible exception of citric, may be treated as dibasic. Thus the first dissociation of orthophosphoric acid is so much greater than the second that $NaH_2PO_4$ may be treated as a dibasic acid.

The abscissæ of some of the curves given in this book are values of R (defined above). The other unit of abscissæ, *i.e.*, the percentage neutralised of the total mols of acid present, is obviously equal to $\frac{100R}{n}$, where "$n$" is basicity of the acid.

For solutions of moderate concentration NaHA and $Na_2A$ in the third terms (which are only correction terms under these conditions) may be obtained with sufficient accuracy from the amounts of acid and alkali taken. This can no longer be done when the solutions are very dilute. In this case it may be shown by substitution in the original ionic equations that

$$[HA'] = [NaHA] = \frac{K_1C}{K_1 + [H\cdot]} \text{ (more acid solutions)}$$

and

$$[A''] = [Na_2A] \quad = \frac{K_2C}{K_2 + [H\cdot]} \text{ (more alkaline solutions).}$$

These terms containing the total concentration C are thus introduced at dilutions at which the solution is less strongly

self-regulating, *i.e.*, those in which [H·] is no longer exclusively determined by R but is also strongly influenced by C. For these dilutions $\alpha_1$, etc., are practically equal to 1,

and
$$R = \frac{1 + \frac{2K_2}{[H\cdot]} + \frac{K_w(K_1 + [H\cdot])}{[H\cdot]K_1C}}{1 + \frac{K_2}{[H\cdot]} + \frac{[H\cdot]}{K_1}} \quad . \quad . \quad (2a)$$

or
$$R = \frac{2 + \frac{[H\cdot]}{K_2} + \frac{K_w(K_2 + [H\cdot])}{[H\cdot]K_2C}}{1 + \frac{[H\cdot]}{K_2} + \frac{[H\cdot]}{K_1K_2}}$$

For an application of these results, see sections on carbonic acid.

*The Course of a Titration.*

The main object of a titration is usually best subserved by the addition of approximately equivalent amounts of alkalies or acids, since the neutralisation curves are most steeply inclined at these points.

The problem of securing not only a sharp but also a stoichiometrically accurate titration in any given case may be solved by a study of the neutralisation curves of this chapter and of the indicator functions of Chap. IV.

The sharpness of a titration may be defined as the closeness (in terms of equivalents per cent. of added alkali or acid) with which a given value of [H·] (the end-point) can be reproduced with the aid of the colour changes of indicators. This sharpness, then, depends upon two equilibria :—

(*a*) The [H·] function of the acid and alkali.

(*b*) The [H·] function of the colour change.

(*a*) Other things being equal, the stronger the acid or base, and the steeper the neutralisation curve, the sharper

is the titration. Indicators may be used which change far from the neutral point either on the acid or alkaline side, or which require a wide range of [H·] in order to complete their change, *e.g.*, litmus; because in this neutral part a very small excess of acid or base changes the hydrion concentration by several powers of 10.

According to the properties summarised in this chapter, p. 232, weaker acids or bases can still be titrated with moderate sharpness, but here more attention must be paid to the choice of indicators, as the steep part of the curve includes a more limited range of [H·] on the acid or alkaline side of the neutral point. The very weakest acids and bases only show a steep curve at the beginning of the titration which obviously cannot be chosen as an end-point. The inclination of the curve to the horizontal at the end-point is still not very great, but is sometimes sufficient with the precautions mentioned under (*b*).

(*b*) The range of hydrogen exponent which is required to complete the colour change is graphically expressed by the width of the bands in the card of indicator changes. The values of the hydrogen exponents on the sides of the card are on the same scale as those on the neutralisation curves. If it is desired to determine the percentages of neutralisation of 0·1 N. acetic acid which are within the phenolphthalein range, the card is applied to diagram so that the edge of the former is an ordinate of the latter, and the higher limit of [H·] (lower of $-\log$ [H·]) just touches the curve. The equivalents per cent. of added alkali are then read off; the card is moved until now the lower limit of [H·] on the edge touches the curve, and the alkali added is again read.

The importance of titrating to standard tint in the case of weak acids and bases will at once be evident. Even the most sensitive indicator covers a comparatively wide range of $-\log$ [H·], but by a colorimetric match this is reduced

to much narrower limits. This narrower band to which the total colour change can be confined by colorimetric methods should be chosen so as to coincide with the indicator function of Noyes (Chap. IV., p. 171). As stated, the greatest sensitivity of a one-colour indicator is found on the side of weaker colour.

But other reasons discussed in that place would point to the middle of the transformation interval as most convenient on the whole if no colorimetric match is made. Titration to standard tint does away with the disadvantage of wide range indicators. The optimum tint is that at which the colour is rather weak but can be seen without very close attention (see Chap. IV.). The accuracy of a titration may be defined by the number of drops of alkali or acid, expressed as a fraction of the total volume added, which are required to produce the end-point change. Since the choice of indicators is now large, their change interval is known, and any part of this interval may be chosen by means of comparison solutions, it is evident that the stoichiometrical accuracy may be made very high. Practically, however, the number of indicators used in an analytical laboratory is usually limited by custom, and the colorimetric method is rejected, as it takes too long. It is then desirable to decide as exactly as possible what are the stoichiometrical errors of titrations as usually carried out. A clear survey of the standards used in volumetric analysis and an explanation of constant errors may be obtained with the help of the preceding considerations.

Since the point of stoichiometrical corresponds to that of absolute neutrality for mixtures of strong acids and strong bases, neutral point indicators would allow the titration to be carried out with absolute accuracy, were it not that they are too sensitive to traces of weak acids or bases that may be present. In practice titrations are always made to the

acid or alkaline side, according to the theory of p. 250, this chapter. This introduces a small error which is responsible for the fact that the same titration gives results affected with different constant errors according to the indicator used. If the change-point of methyl orange is taken as 3·7, it is seen from Diagram p. 226 that the percentage of the acid actually neutralised at this exponent is 98·5, or the result is about 1 per cent. too low. On continuing the neutralisation curve on the alkaline side to the extent of ·1 per cent. excess alkali (at $a_B = 0{\cdot}9$, $-\log [H^{\cdot}] = 11{\cdot}10$), it is seen that the change-point of phenolphthalein corresponds to not more than 0·1 per cent. excess alkali.

These statements are confirmed on the whole in analytical chemistry, although only approximately, as is to be expected, since indicator, concentration tint of end-point, etc., vary widely and are rarely stated with sufficient detail.

The difference between the phenolphthalein and methyl orange titration results and the stoichiometrically accurate values was determined by Kuster and Gruters, *Zeitsch. anorg. Chem.*, 35, 454 (1903). The points of absolute neutrality were found by the minima of conductivity.

There were taken, *e.g.*, 20 c.c. of 0·2 N. $Ba(OH)_2$, and these were titrated with 0·1 N. HCl.

| C.c. HCl for Phenol-phthalein. | C.c. HCl for Minimum Conductivity. | C.c. HCl for Methyl * Orange. |
|---|---|---|
| 39·95 | 39·97 | 40·21 |
| 40·0 | 40·03 | 40·23 |

Thus on the average the equivalents of acid required for the phenolphthalein were 0·055 per cent. in defect, and for the methyl orange 0·55 per cent. in excess of the true amounts. When NaOH was used instead of $Ba(OH)_2$ the

* The further experiments of Kuster and Gruters show that the neutral tint of methyl orange actually was at 4·22 and not 3·7, but this makes no material difference in the above calculations.

acid used for phenolphthalein was 0·59 c.c. or equivalents per cent. short of the minimum, a difference which is probably due to the presence of carbonate. If this were so, its influence is also to be seen in the methyl orange titre which is now only 0·4 per cent. too high. The curve is almost identical in the case of other strong acids and bases, and hence the constant error is the same for any particular indicator. If an accuracy of $\pm$ 1 per cent. is sufficient and is required from the results without correction, all indicators turning between about 4·0 and 10·0 may be employed if the solutions are decinormal or upwards. When the concentrations are lower, however, the hydrion or hydroxylion error (see p. 253) begins to have an effect. This may be seen by glancing at Diagram p. 232 which corresponds nearly to the conditions when 0·01 N. acid is being titrated with 0·01 N. alkali and *vice versâ*. The error due to employing an indicator which changes at these limits (4·0 and 10·0) is now about 2 instead of 1 per cent. Indicators turning at or about 5·0 and 9·0 will now be required for an accuracy of 1 per cent. It might be supposed that the neutral point indicators could be used, but this is not the case, since their changes are not sharp under these conditions. Iodeosin is recommended by Glaser as giving sharp and exact titrations in dilute solution.

Tables of the actual number of c.c. required when the titration is carried out in either direction have been constructed by Glaser, "Indikatoren" (*Scholtz Arch. d. Pharm.*, 242, 575 (1904)), and are to be found in other works of reference.

*About Half-normal Alkali + Normal HCl.*

For every 10 c.c. of normal alkali there is required with methyl orange 10·05, with phenolphthalein 9·95, with phenacetolin 10·03 c.c. of N. acid.

*About* $\frac{1}{60}$ *N. Sulphuric Acid + Decinormal Alkali.*

Each 10 c.c. of 0·1 N. sulphuric acid requires c.c. alkali—

| | |
|---|---|
| Methyl and ethyl orange | 9·9 |
| Congo, cochineal, lacmoid, litmus, fluorescein, phenacetolin | 10·0 |
| Gallein | 10·05 |
| Rosolic acid and tropaolin OOO | 10·07 |
| Alizarin, curcuma, phenolphthalein α naphthol benzoin | 10·10 |

*About* $\frac{1}{600}$ *N. Sulphuric Acid +* $\frac{1}{100}$ *N. Sodium Hydroxide.*

Each 10 c.c. of 0·01 N. $H_2SO_4$ requires c.c. alkali—

| Methyl orange. | Congo. | Lacmoid. |
|---|---|---|
| 9·55 | 9·75 | 9·90 |
| **Litmus.** | **Phenolphthalein.** | |
| 10·30 | 10·70 | |

*Hydrochloric Acid* 0·01 *N. + Sodium Hydroxide* 0·01 *N.*

| | Methyl orange. | Paranitrophenol. | Iodeosin. |
|---|---|---|---|
| C.c. alkali to 10 HCl | 9·3 | 9·9 | 9·7 |
| C.c. acid to 10 NaOH | 10·7 | 10·0 | 9·8 |

| | Litmus. | Rosolic acid. | Phenolphthalein. |
|---|---|---|---|
| C.c. alkali to 10 HCl | 9·9 | 9·9 | 10·1 |
| C.c. acid to 10 NaOH | 9·85 | 9·85 | 9·9 |

The reasons for the discrepancies of these tables follow from the results contained in this and the preceding chapters.

*The Titration of Strong Acids (Bases) in the Presence of Weak Bases (Acids).*

Since in the titration of a strong acid with a strong base either an acid or alkaline end-point may be used at will, it is possible to titrate only the strong constituent of a salt, neglecting the other. If the latter is exceedingly weak, as in the case of aluminium salts, the base produced in the addition of alkali does not give any appreciable [OH'], and any neutral or alkaline indicator may be used. If the base is somewhat stronger as in the case of the chlorides of aniline or paratoluidine, the correct end-point is alkaline, and phenolphthalein will serve, as this is unaffected by the free bases. A still stronger base will require a still higher [OH'], *i.e.*, between $10^{-3}$ and $10^{-4}$ for free ammonia. The titration of the hydrochloric acid alone, then, in ammonium chloride would not give a sharp end-point, but by matching against solutions of known alkalinity in presence of, *e.g.*, alizarin yellow, it should be possible to obtain results accurate to a few per cent.

So, also, the alkali alone in a salt of a weak acid, such as sodium borate, may be determined by titration. The stronger the acid with which the base is combined, the more acid will have to be the end-point. Among examples of this numerous class of titrations are those of total alkali in carbonates and hydrosulphides.

*Weak Acids and Bases which give Univalent Ions.*

Since in the case of weak acids the correct end-point is on the alkaline side, an alkaline indicator is the best, although in case of need an acid indicator might sometimes be used.*

* Thus with a constant correction, an indicator turning at 6 might be used in the titration of acetic acid, while the weaker acid indicators such as methyl red and *p*-nitrophenol might be used in the titration of acids of intermediate strength, such as formic.

From the neutralisation curve of 0·1 N. acetic acid it is seen that the first appearance of colour with phenolphthalein (8·3) corresponds to a deficit of alkali of about 0·5 per cent. below that required for sodium acetate, which should give a full red. By employing only a little of the indicator and titrating to a full pink, practically exact results are obtained. Acids as weak as phenol will evidently not give sharp titrations under any circumstances. The correct end-point lies at about 10·8. The best indicator may be chosen from the tables or graphically by the card as already described (p. 206).

Since the steepest part of the neutralisation curve of weak bases is on the acid side, an indicator of acid exponent must be employed in the titration of ammonia, etc.* At 3·7 (methyl orange) decinormal ammonia has been slightly over-neutralised, while at 5·2 (middle point of methyl red) the titration is practically exact. Bases such as aniline can still be titrated with indicators of this class, but as the constant falls the conditions become less favourable, until with bases as weak as p. chloraniline there is no sharp titration possible.

### *The Titration of One Acid or Base in a Mixture.*

If there is a considerable difference between the strengths of two acids it is often possible by a suitable choice of indicator to determine the stronger one separately. In order to make the choice on rational grounds it is necessary to know the forms of the separate neutralisation curves. If the form of the curve of the two acids mixed in the required proportion is known the problem is, of course, completely solved. This knowledge is seldom available,

* An indicator of alkaline exponent, such as phenolphthalein, changes, but not sharply, when about 90 per cent. of the equivalent amount of acid has been added.

but an approximate solution is obtained as above, or even from the dissociation constants. It is only necessary to choose as the end-point a value of [H·] which is higher than that which could be given by the weaker of the two acids in any probable concentration. Thus, suppose it is required to titrate formic acid, $K = 2{\cdot}14 \times 10^{-4}$ in the presence of phenol $K = 1{\cdot}3 \times 10^{-10}$ (Thiel, see p. 231).

It is easy to ensure that the solution shall not be more than 0·1 N. with respect to the phenol. The value of [H·] due to this cannot therefore be greater than $10^{-5{\cdot}45}$. The formic acid curve at this point is still too little inclined to the horizontal for a sharp titration, consequently the titration must be supplemented by colour matching. A standard tint suitable for this purpose is that of p. nitrophenol in water, 3 drops of the indicator (3·5 grams in 100 c.c. of alcohol) to 200 c.c., or methyl red 15 drops of the indicator (0·1 per cent. weakly alcoholic aqueous solution) to 200 c.c. The colour of the former is greenish yellow and that of the latter reddish yellow, and neither is affected by 0·1 N. phenol. The results must, of course, be multiplied by a factor which expresses the degree of neutralisation at this value of [H·]. It is easily obtained by titrating the formic acid without phenol, first to the ordinary phenolphthalein end-point, and then to the colour match.

By this means a sufficient accuracy may be obtained. The results were practically independent of the ratio phenol to formic acid when this was varied between 0·38 and 15·0.

The detection of mineral acids in the presence of acetic has been already described. The titration of the former, if present in considerable amount, could be undertaken with an indicator of sufficiently high acid exponent. The main conditions for success in this kind of titration are—

(1) The chosen end-point cannot be too far from the neutral-point for the reason given on p. 253.

(2) The concentration of the weak constituent must be kept below the limit assigned in planning the titration.

| Total Volume. | Millimols HCOOH. | Millimols $C_6H_5OH$. | Indicator. | C.c. approximately 0·5 N·NaOH. | |
|---|---|---|---|---|---|
| | | | | Found. | Calculated. |
| 200 | 10 | 15 | Paranitrophenol | 22·60 (22·59 to 22·61) | 22·60 |
| 200 | 2 | 15 | ,, | 4·51 | 4·52 |
| 200 | 10 | 7·5 | Methyl red . | 23·85 | 23·88 |
| 190 | 10 | 3·8 | ,, ,, . | 23·89 | 23·88 |

*The Titration of Polyhydrion Acids.*

The problem of titrating separately the successive hydrions of an acid which dissociates in two or more steps is essentially the same as that of titrating each acid in a mixture (in equivalent proportions) of monohydrion acids with different constants. The problem is solved by the neutralisation curves of the acids (see phosphoric acid, etc.), and graphically by the application of the card of indicators to the curves (p. 242).

*The Theory of Titration Errors.*

While the accuracy of titrations is often sufficiently known from the neutralisation curves at average dilution and may in all cases be strictly controlled by empirical methods, yet it is often desirable to be able to predict the exact error, and the best concentration of the standard

solutions, etc., in any given case. The theory of titration formulated by Bjerrum (Titrierungen) will be found a most powerful aid towards these objects. It also makes possible further advances in volumetric analysis. This theory does not include a consideration of "drop errors" or errors in reading burettes, etc. (since these are adequately dealt with in text-books of physical methods and of volumetric analysis), but only those which are due to the nature of the electrolytic equilibria. The theory depends mainly upon the existence of dissociation constants.

It is assumed then that the titrating liquid (called for convenience the titrant) can be added in the exact amount required to the liquid which is being titrated (called the titree). The error in practice is about 0·01 to 0·03 c.c. by volumetric methods, or somewhat less with weight burettes (Washburn, *J. Amer. Chem. Soc.*, 30, 31 (1908)).

The calculated error when smaller than this has, of course, no significance in actual work. In the calculations dealing with the electrolytic equilibria it is assumed that all strong acids, alkalies, and salts are completely dissociated, and that the dissociation of the weak ones can be expressed by constants.

In a completed titration there will be present, besides the salt formed, certain concentrations of $H^{\cdot}$, $OH'$, HA, and BOH. According to the laws of chemical equilibrium none of these molecular species can ever completely vanish, but at least half of them may usually be neglected.

Since it is a fundamental rule to use always a strong base or acid as the titrant, two of these concentrations will be considerable and two negligible. If a weak acid is being titrated [HA] and [OH′], and if a weak base is being titrated [BOH] and [H·], will be considerable. The error in the titration will be equal to the difference between total base and total acid in the solution at the end-point. If V

is the volume of this (in c.c.), then the error for a weak acid is—

$$\frac{V}{1000}([OH'] - [H\cdot] - [HA]) \text{ equivalents} \quad . \quad (1a)$$

and that for a weak base is—

$$\frac{V}{1000}([H\cdot] - [OH'] - [BOH]) \text{ equivalents} \quad . \quad (1b)$$

A positive error in both cases denotes an excess of the titrant in equivalents beyond the amount required for stoichiometrical neutrality. It is more convenient, however, to express the error as c.c. of the solution (of normality "$n$") which is being used for the titration. Remembering that $x$ gram equivalents are equivalent to $\frac{1000x}{n}$ c.c. of an "$n$" normal solution, it is evident that the error may be expressed as—

$$\frac{V}{n}([OH'] - [H\cdot] - [HA]) \text{ c.c.} \quad . \quad . \quad (2a)$$

for the titration of an acid, or

$$\frac{V}{n}([H\cdot] - [OH'] - [BOH]) \quad . \quad . \quad (2b)$$

for the titration of a base.

And the most general expression for the error "$e$" of all solutions is—

$$e = \frac{V}{n}([OH'] - [H\cdot] - [HA] + [BOH]) \quad . \quad (2)$$

the signs being changed in the titration of a base.

The total error may thus be resolved into—

(1) A hydrion or hydroxylion error.

(2) An acid or base error.

(1) At the point of absolute neutrality the $H\cdot$ error

exactly compensates the OH′ error. With acid end-points (exponent less than 7) the former, with alkaline end-points the latter, must be considered.

The greater the volume of the "titrate," the greater must be the number of c.c. of titrant which are required to produce a given [H·] or [OH′]. Thus, if in a solution of volume 100 c.c. the error is to be less than 0·01 c.c. of 0·1 N. titrant, then the [H·] or [OH′] must not be greater than $1 \times 10^{-5}$.

For

$$e = 0{\cdot}01 = \frac{V}{n}[H\cdot] = \frac{100}{0{\cdot}1} \times [H\cdot].$$

If the [H·] at the end-point as in this example must lie between $1 \times 10^{-5}$ and $1 \times 10^{-9}$, then no indicator of smaller $p_I$ than that of methyl orange and of larger $p_I$ than (a little) phenolphthalein can be used. But the volume is more usually 50 than 100 c.c., and the limits for 0·1 N. titrant in this volume will be $2 \times 10^{-5}$ and $5 \times 10^{-10}$. So also if a 0·2 N. titrant is used in 50 c.c. the limits are further extended to $4 \times 10^{-5}$ and $2{\cdot}5 \times 10^{-10}$.

*The Acid or Base Error $e_{HA}$ or $e_{BOH}$.*

If the total concentration of acid in any form is written $C_A$, then

$$e_{HA} = \frac{V}{n}[HA] = \frac{V}{n}C_A\frac{[H\cdot]}{[H\cdot] + K\cdot}$$

But $VC_A$ = total milli equivalents of acid present,

and $\therefore \frac{VC_A}{n}$ = number of c.c. of the titrant equivalent to the total acid.

Calling this $T_A$ = the titration value of the total acid present,

$$e_{HA} = T_A\frac{[H\cdot]}{[H\cdot] + K} = T_A\frac{[H.]}{K_A} \quad . \quad . \quad (3a).$$

For if this error is to be small, [H·] must be small compared to K.

" The acid error is equal to the number of c.c. of titrant required for the titration multiplied by the ratio between [H·] at the end-point and the dissociation constant of the acid " (Bjerrum).

In the same way it may be shown that the base error

$$e_{\mathrm{BOH}} \text{ is } T_B \frac{[OH']}{K_B} \quad . \quad . \quad . \quad (3b).$$

and this is smaller the lower is [OH'] at the end-point.

The equations (2*a*) and (2*b*), p. 252, may now be written—

$$e = \frac{V}{n}[OH'] - \frac{V}{n}[H\cdot] - T_A \frac{[H\cdot]}{K_A} \quad . \quad . \quad (4a).$$

$$e = \frac{V}{n}[H\cdot] - \frac{V}{n}[OH'] - T_B \frac{[OH']}{K_B} \quad . \quad (4b).$$

The acid error for a given $K_A$ is diminished in proportion to [H·]. A limit, however, to the diminution of [H·] is imposed by the condition that [OH'] cannot exceed a certain value, *e.g.*, $1 \times 10^{-5}$ in the example already given. If the acid error is not to exceed 1 per cent. of the acid present, then $1 \times 10^{-9}/K$ must not exceed 0·001, *i.e.*, K must not be less than $1 \times 10^{-6}$. It follows that since most organic carboxylic acids fulfil this condition they can be titrated accurately with phenolphthalein. Similarly the base error is smaller the lower the [OH'] is at the end-point. The lowest value permissible on account of the H· error is $1 \times 10^{-9}$. Therefore the constant $K_B$ must not be less than $1 \times 10^{-6}$ if an accuracy of 1 per cent. is required.

In general, a weak acid should be titrated to the lowest [H·], which does not give a hydroxyl error above the required limits, and a similar rule holds for the titration of

a weak base. As these limits are relaxed, the total volume of the titrate is diminished and the concentration of titrant is increased, so, in accordance with the equations, wider limits of [H·] and [OH′] can be used, and therefore weaker acids and bases can be titrated. The conditions of titration may then be stated in relation to the magnitude of the dissociation constants.

If the normality of the titrant is 0·1 or over and the volume of the titrate is 100 c.c. or under, and the acid error $e_{HA}$ is not to be more than 1 per cent., then K must be at least 1,000 times greater than [H·]. But if the OH′ error is not to be greater than 0·01 c.c. of titrant, then the minimum value of [H·] is $1 \times 10^{-9}$. Therefore the maximum value of K is $1 \times 10^{-6}$. Other conditions are tabulated below. Thus if an accuracy of only 1 per cent. on the acid or base titre is required, the conditions (2) in the table would allow acids or bases to be titrated with constants of $1 \times 10^{-8}$, and finally under (4) it would be possible to titrate the very weakest acids and bases down to $1 \times 10^{-10}$, *e.g.*, phenol and aniline.

| Volume of titrate V. | Normality of titrant *n*. | Maximum [H·] or [OH′] error $\frac{V}{n}$ [H·] or $\frac{V}{n}$ [OH′]. | Permissible range of [H·]. | Lowest value of $K_A$ or $K_B$. |
|---|---|---|---|---|
| (1) 100 | 0·1 | 0·01 | $10^{-5}$ to $10^{-9}$ | $10^{-6}$ |
| (2) 10 | 0·1 | 0·01 | $10^{-4}$ to $10^{-10}$ | $10^{-7}$ |
| 100 | 1·0 | 0·01 | | |
| 100 | 0·1 | 0·1 | | |
| (3) 10 | 1·0 | 0·01 | $10^{-3}$ to $10^{-11}$ | $10^{-8}$ |
| 100 | 1·0 | 0·1 | | |
| (4) 10 | 1·0 | 0·1 | $10^{-2}$ to $10^{-12}$ | $10^{-9}$ |

It might be thought that since the OH′ and acid errors, the H· and base errors have opposite signs, they might compensate one another at a particular value of [H·]. For in the equation (7) of p. 261, this chapter, all the positive errors are directly, and the negative errors are inversely, proportional to [H·], and the equation

$$\frac{K}{[H\cdot]} + K'[H\cdot] = 0$$

always has a real positive root when K and K′ are positive.

In practice, however, the compensation is impossible, since [H·] at the end-point cannot be obtained exactly, but only a range of [H·] within certain limits. Since [H·] occurs in the numerator of the positive, and in the denominator of the negative, terms any variation from the correct value $[H\cdot]_T$ will produce a considerable positive or negative error. The [H·] interval of an ordinary titration may be taken as from $\frac{1}{2}H_T$ to $2[H\cdot]_T$, and therefore the total error at each end of the interval will be greater than the value of each compensating error "$e$" at $[H\cdot]_T$. It will be $\frac{3}{2}e$ at $\frac{1}{2}[H\cdot]_T$ and $-\frac{3}{2}e$ at $2[H\cdot]_T$.

Since the compensation only removes 25 per cent. of the total error (the sum of + and − single errors) it is best to take care that the sums of both the positive and the negative errors is within the limit of the accuracy required.

*The Correct Volumes of Titrated Solution.*

Since according to equations (4*a*) and 4*b*), p. 254, the total volume of titrated liquid only affects the H· and OH′ error, it is possible to state the maximum volumes which should

be employed for a given accuracy if the normality of the titrant is given. They are stated in the table below, under the headings of the normalities of the titrants.

| [H·]. | Maximum Volumes for the Normalities. | | |
|---|---|---|---|
| | $n = 1$. | $n = 0{\cdot}1$. | $n = 0{\cdot}01$. |
| $10^{-3}$ | 10 c.c. | 1 c.c. | 0·1 c.c. |
| $10^{-4}$ | 100 c.c. | 10 ,, | 1·0 ,, |
| $10^{-5}$ | 1 litre | 100 ,, | 10 ,, |
| $10^{-6}$ | (10 ,, ) | (1 litre) | (100 ,, ) |
| $10^{-8}$ | (10 ,, ) | (1 ,, ) | (100 ,, ) |
| $10^{-9}$ | (1 ,, ) | 100 c.c. | 10 ,, |
| $10^{-10}$ | 100 c.c. | 10 ,, | 1 ,, |
| $10^{-11}$ | 10 ,, | 1 ,, | 0·1 ,, |

The volumes in brackets cannot be used in practice, since the ordinary impurities in the distilled water (about $1 \times 10^{-5}$ N.) affect [H·] values which are so near the neutral point. On this account the total volume of the solution should not be greater than 1,000 $n$. No general answer can be given to the question, "What is the best normality of titrant?"

If the amount of acid or base is fixed, and the volume of the titrated solution is mainly dependent on the volume of the titrant, as in titrating solids or very concentrated solutions, the percentage error is not altered by altering $v$ or $n$, since each varies inversely as the other. If the amount of acid or base to be titrated may be made as large as required, then it is advantageous to use concentrated solutions, and just that volume at which the errors of measurement become negligible, *i.e.*, about 20 to 30 c.c. usually.

If only a small amount of acid and base is available for each titration, then it is better to use more dilute solutions of the titrant, as thus the necessity for very close reading of burettes is avoided. The gradual character of the colour change is not objectionable within limits, and may even lead to an increased accuracy if comparison solutions are used. The final volumes must in all cases be kept within the limits of the table on p. 257, above.

If the titrant is very dilute an allowance must be made for the amount required to produce the change in the amounts of indicator used.

| Indicator. | Phenolphthalein. | |
|---|---|---|
| Amount added to 100 c.c. / C.c. of 0·1 N. titrant | 0·4 c.c. of 0·1 per cent. / 0·025 | 0·7 c.c. of 1·0 per cent. / 0·44 |

| Indicator. | Methyl Orange. | Methyl Red. |
|---|---|---|
| Amount added to 100 c.c. / C.c. of 0·1 N. titrant | 0·1 c.c. of 0·1 per cent. / 0·003 | 0·1 c.c. of 0·1 per cent. / 0·003 |

*The Effect of Temperature upon Titrations.*

The theoretical effect of rise of temperature upon all constants, whether of indicators or other acids and bases, has been stated on p. 166, Chap. IV. It has been shown by Bjerrum that the limiting constants of acids and bases which can be titrated with a given accuracy must be greater

at higher temperatures and may be smaller at lower temperatures. Thus, if the conditions of accuracy of p. 253 are observed the $[H^{\cdot}]$ must lie between $1 \times 10^{-5}$ and $1 \times 10^{-9}$ in order that the $H^{\cdot}$ or $[OH']$ error may be less than 0·01 c.c. of the 0·1 N. titrant.

Now if $T_A$ in equation (3a), p. 253, is 10 c.c. and $[OH'] \leqq 1 \times 10^{-5}$ and also $e_{HA}$ (acid error) is $< 0{\cdot}01$ c.c.,

$$\text{then } 0{\cdot}01 \begin{matrix} = \\ > \end{matrix} \frac{10 \times K_W}{[OH']K_A} \text{ or } K_A > \frac{10 \times K_W}{0{\cdot}01 \times 10^{-5}} \text{ or } K_A > 10^8 K_W.$$

For the titration of a base under similar conditions it is necessary that $K_B > 10^8 K_W$.

In the tables on p. 6, Chap. I., it is seen that $K_W$ (at 0°) $= \frac{1}{5} K_W$ (at 18°), $K_W$ (at 100°), 100 $K_W$ (at 18°). Therefore acids and bases which can be titrated with the above accuracy at 100° must have constants greater than (50 to 70) $\times 10^{-6}$, while if the titration is at 0° the constants need only be $>$ (0·09 to 0·14) $\times 10^{-6}$. The increase in the constants of acid or base has the opposite effect to that of the water constant, while the increase in the indicator constants may have an effect in the opposite or in the same direction (see p. 166). Although these effects on the end-point of the titration will be relatively slight, yet changes such as those mentioned on p. 167, Chap. IV., should be taken into account. It is usually better to avoid titrations in hot solutions, especially as these can generally be rendered unnecessary by an appropriate choice of indicator. Titrations at about 0° are, on the other hand, to be recommended except where time reactions are involved (see Carbonic Acid, p. 319).

### *Titration of a Mixture.*

If a number of acids (or bases) with different dissociation constants are present together in the solution it is often possible to find the sum of their equivalents by titration.

The errors [HA] and [BOH] which express the amounts of free acid or base left in the solution at the end simply need to be replaced by $\Sigma$[HA] and $\Sigma$[BOH], and these in their turn may be replaced by

$$\Sigma T_A \frac{[H^\cdot]}{K_A} \text{ and } \Sigma T_B \frac{[OH']}{K_B}.$$

So that the total error for a number of acids or bases of which, say, the acids are to be titrated is—

$$e = \frac{V}{n}[OH'] - \frac{V}{n}[H^\cdot] + \Sigma T_B \frac{[OH']}{K_B} - \Sigma T_A \frac{[H^\cdot]}{K_A} \quad . \quad (5)$$

Now let there also be present a number of acids H$a$ and bases $b$OH, none of which are to be included in any titration. If they remain in the undissociated condition at the end-point the titration is successful, for they are wholly omitted. But so far as they form ions $a'$ or $b^\cdot$ they cause an error. An equation may then be written for the total error including these :—

$$e = \frac{V}{n}([OH'] - [H^\cdot] - \Sigma[HA] + \Sigma[a'] + \Sigma[BOH] - \Sigma[b^\cdot]) \quad . \quad (6)$$
$$\qquad 1 \qquad 2 \qquad 3 \qquad 4 \qquad 5 \qquad 6$$

As before, terms 2, 5, 6 are omitted in the titration of weak acids only, 1, 3 and 4 in the titration of weak bases only. An error consisting in the addition of too little base in the first case is taken as negative $-\Sigma$[HA], an error of too little acid in the second is taken as positive $+\Sigma$[BOH]. The signs of $\Sigma$[HA] and $\Sigma[a']$ differ because titratable acid in the undissociated state means a defect of alkali, while untitratable and in the ionic state means excess of alkali. From the equations of dissociation—

$$a' = C_a \frac{K_a}{[H^\cdot] + K_a} \text{ and } b^\cdot = C_b \frac{K_b}{[OH'] + K_b}.$$

And if $[H^{\cdot}]$ is to be chosen so that these errors are small, then $K_a$ and $K_b$ must be small compared to $[H^{\cdot}]$.

So, substituting the values $a' = C_a \frac{K_a}{[H^{\cdot}]}$, etc., and also $\frac{V}{n} C_a = T_a$, the equation becomes—

$$e = \frac{V}{n} \frac{K_W}{[H^{\cdot}]} - \frac{V}{n}[H^{\cdot}] - \Sigma T_A \frac{[H^{\cdot}]}{K_A} + \Sigma T_a \frac{K_a}{[H^{\cdot}]} + \Sigma T_B \frac{K_W}{K_B[H^{\cdot}]} - \Sigma T_b \frac{K_b[H^{\cdot}]}{K_W} \quad . \quad . \quad (7)$$

The total error on the titratable acids is thus equal to the sum of the separate errors due to each according to its concentration and constant. As the absolute error $T_A \frac{[H^{\cdot}]}{K_A}$ is proportional to $T_A$, the titration equivalent of the acid present, it is clearly diminished if the acid is present in very low concentration. Therefore an acid present in amount equal to only 1 c.c. of the titrant may have $k$ only 10 times the value of $[H^{\cdot}]$ and still only cause an error of 0·1 c.c. on the whole titration. The proportionate error on this acid alone would, however, be great. Similarly the acids that are not to be titrated may have dissociation constants greater than one-thousandth of $[H^{\cdot}]$ without appreciably affecting the results, if they are present in very low concentration. Acids which are on the doubtful area between those which can and those which cannot be titrated at a given $[H^{\cdot}]$ (see diagram, p. 263) should be kept in as low concentrations as possible, for their effect in dulling the end-point is most deleterious. In fact, an acid of which $K = [H^{\cdot}]$ acts as a hydrion regulator (see Chap. V., p. 191), and if present in moderate concentration flattens the neutralisation curve so as to make a sharp titration impossible.

The chief use of these equations is to decide whether it is possible to titrate a given mixture of acids and bases, and if the titration is possible, to decide what is the right [H·] to take as the end-point.

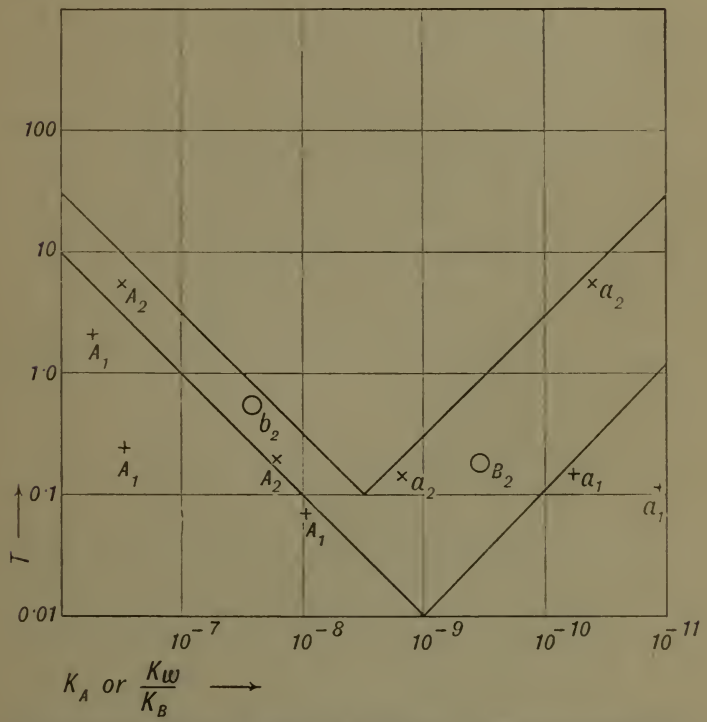
Taking as an example a mixture of acids for which the titration error is not to exceed 0·01 c.c. of the titrant, it is necessary that—

$$e\ (= 0{\cdot}01) \underset{<}{=} T_A \frac{[H\cdot]}{K}.$$

The correct value of [H·] which must be chosen in order that this error may not be exceeded is easily found from a diagram (p. 263 below) in which the titration equivalents of each acid $T_A$ are plotted on a logarithmic scale (as ordinates) against values of $K_A$, likewise on a logarithmic scale (as abscissæ). The $T_A$, $K_A$ points are marked on this diagram. A point is then sought on the 0·01 ordinate level from which two lines may be drawn at 45°, above which will lie none of the points already marked. Below the line on the left lie all acids $+ A_1$ which are titratable with the required accuracy at the value of [H·] given by the abscissa which is marked off by the point of intersection of the lines. Below the line on the right lie all acids $+ a$ which do not affect the titration beyond the chosen limit of error. For example, if the intersection of the lines is at $e = 0{\cdot}01$ and $[H\cdot] = 1 \times 10^{-9}$, then the concentrations and constants of all titratable acids are included in the relation $\frac{T_A}{K_A} > 1 \times 10^{-7}$ ($\log T_A - \log K_A > 7$), while the acids which are not to be titrated are included in the relation $T_a K_a < 10^{-11}$ ($- \log T_a - \log K_a > 11$).

Points in the area above the lines correspond to acids of which the amounts and constants are such that they falsify the titration by an error exceeding 0·01 c.c. If now it is

desired to include those shown by × $A_2$ on the left, and exclude those shown by × $a_2$ on the right, then a new [H·] may be required and the accuracy will have to be less. If




The Titration of Acids and Bases in different amounts and with different Constants in presence of one another.

the latter may now be up to 0·1 c.c. then the minimum of $\frac{T_A}{K_A}$ may be greater by a power of 10, *i.e.*, may equal $1 \times 10^8$. The maximum value of $T_A K_A$ may now be $10^{-10}$ instead of $10^{-11}$, and stronger acids may therefore be excluded from the titration. The same diagram may be used for bases,

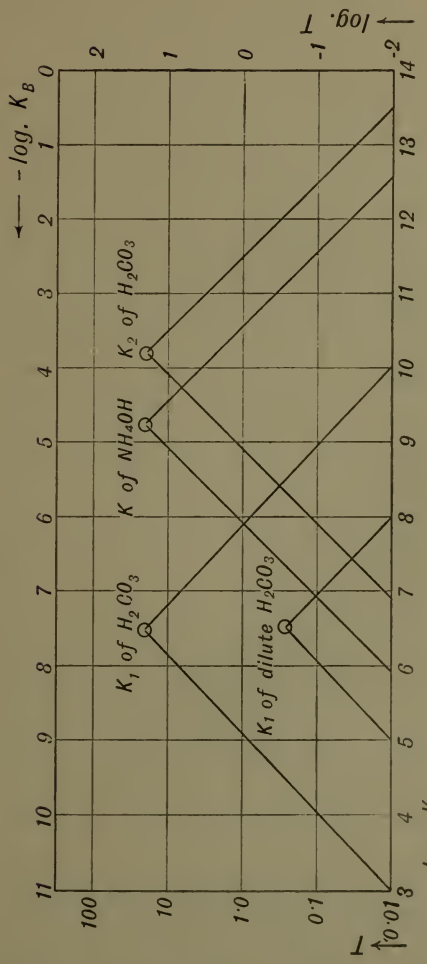
$K_W/K_B$ being written for $K_A$, or a reversed scale of abscissæ may be used for $K_B$ (see diagram, p. 265).

In the diagram it is shown that the left-hand area contains acids + A which are, and bases ⊙ *b* which are not, to be included in the titration, while the right-hand area contains bases ⊙ B which are, and acids + *a* which are not, to be included.

The most usual problems of the analyst are probably (1) to titrate one by one two or more weak acids or bases in a mixture, or (2) to titrate the different steps of a polyhydrion acid or a polyhydroxylion base. Both may be dealt with by the same methods. Lines are drawn downwards through the K, T points at 45° to the axes of abscissæ, and the points where these lines intersect give both the best [H·] values for each titration, and the errors to be expected at each end point. Examples are given under the separate acids, pp. 288, 323.

*Titration of Weak Bases in presence of Weak Acids, and vice versâ.*

The titration of ammonia in the presence of carbonic acid is seen to be possible from the curves, because at the [H·] corresponding to the steep part of the ammonia neutralisation the carbonic acid will practically all be present as $H_2CO_3 + CO_2$. The probable accuracy of such a titration is given by the diagram due to Bjerrum. If $H_2CO_3$ and $NH_3$ are both present in amount equivalent to 20 c.c. of the titrant, their K, T points are as shown. The possible titration exponents will lie on the line drawn from K, T at 45° to the left. The K, T points for carbonic acid in concentrations below that given are on the right of this line, and are, therefore, excluded, while $NH_3$ is to the right and is therefore included. The whole of the ammonia may therefore be titrated at an exponent considerably less than 6·52




The Titration of Ammonia in the presence of Carbonic Acid.

(— log $K_1$). If methyl orange 4 is used the volume of titrate should be kept below 50 c.c., and this with 0·2 N. titrant will make the H· error equal to $\frac{50}{0{\cdot}2} \times 1 \times 10^{-4}$

$= 0{\cdot}025$ c.c., the acid error being $\frac{20 \times 3 \times 10^{-7}}{1 \times 10^{-4}} = 0{\cdot}06$ c.c. (see p. 261).

If the amount of $CO_2$ is smaller, then the $T_a$, K point lies lower, and a lower value of $[H^{\cdot}]$ can be used. Thus the amount of $CO_2$ shown by the lower point $x$ ($T_a = 1{\cdot}0$ c.c.) would allow a titration to be carried out at 5 (methyl red), the $H^{\cdot}$ error under the same conditions as above being only $0{\cdot}0025$ and the acid error now $0{\cdot}009$. The titration of $CO_2$ to $Na_2CO_3$ in the presence of $NH_3$ is not possible on account of the magnitude of the $OH'$ error. If, however, both acid and base have constants which are not too low, say $1 \times 10^{\cdot -6}$, then it will always be possible to titrate the acid in presence of the base by ending, say, at $[H^{\cdot}] = 1 \times 10^{-10}$ and the base alone by ending at $[H^{\cdot}] = 1 \times 10^{-4}$.

It would be possible to forecast the best conditions of a great variety of such titrations from the constants of Chap. I.

*Titrations which are to Include or to Exclude Insoluble Acids or Bases.*

Any acid (or base) which is so slightly soluble that the saturated solution is almost completely ionised has a concentration of $H^{\cdot}$ $[OH']$ which is equal to the solubility or to the square root of the solubility product $S_A$ ($S_B$), since

$$S_A = [H^{\cdot}]\,[A'] \text{ and } S_B = [OH']\,[B^{\cdot}].$$

In order that the whole of such an acid should be brought into solution and neutralised it is evident that the $[H^{\cdot}]$ at the end-point must be less than $\sqrt{S_A}$.

The condition is that $[H^{\cdot}]\,[A'] < S_A$.

But $[A'] = \frac{n}{V} T_A$ (see p. 253).

Therefore it is necessary that—

$$[H\cdot] < \frac{V}{n}\frac{S_A}{T_A}.$$

So also in the case of a base that is to be brought into solution and neutralised, it is necessary that

$$[OH'] < \frac{V}{n}\frac{S_B}{T_B}.$$

If, on the other hand, it is desired to carry out a titration in the presence of insoluble acids or bases, without including these, the errors are given by the equations on p. 260.

For an acid

$$e = \frac{V}{n}[a'].$$

Therefore, if the error $e$ is the largest which is permissible,

$$\frac{V}{n}\cdot\frac{S_a}{[H\cdot]} < e.*$$

An example of this given by Bjerrum is the titration of the $HNO_3$ in $AgNO_3$ disregarding the hydroxide formed. The AgOH is a base which is strong, *i.e.*, completely dissociated in solution, but which cannot give a high [OH′] on account of its low solubility $S_b = 10^{-7\cdot65}$ (Noyes and Kohr, *Zeitsch. phys. Chem.* 42,336 (1903)).

The minimum [OH′] is

$$[OH'] > 10^{-7\cdot65}\frac{V}{ne}.$$

If the total volume is 100 cc. and the error is to be not more than 0·02 c.c. of the 1·0 N. alkali used in the titration,

* If the acid is all dissolved at the end-point because the solubility is fairly high or the total concentration low, then the error is, as before in equation (7), p. 261, equal to

$$T_a\frac{K_a}{[H\cdot]}.$$

So also for a slightly soluble base that is not to be titrated—

$$\frac{V}{n}\frac{S_b}{[OH']} < e.$$

then the minimum [OH′] is $10^{-3\cdot95}$. The titration must, therefore, be carried out to a hydrogen exponent 10 (very little phenolphthalein, thymolphthalein, etc.) (see Chap. IV., pp. 156, 157).

This theory could be usefully applied to determining the best conditions of titration of the very slightly soluble alkaloids.

*Titrations which lead to the Formation of Insoluble Salts.*

If to the salt of a very weak acid there is added a kathion which is capable of forming with the anion a very slightly soluble precipitate the effect is to remove this anion from the solution, and therefore from the hydrolytic action of the water. The amount of anion [A′] left in solution is given by the solubility product $[B\cdot]\,[A'] = S$, and therefore [A′] can be reduced still further by adding more of the kathion B· in the form of a soluble salt. By this reduction of [A′] the [OH′] produced by hydrolysis is necessarily much decreased and a titration becomes possible.

The acid error $e$ is given by the equation

$$e = \frac{V}{n} \cdot [A'] \frac{[H\cdot]}{K} \quad . \quad . \quad . \quad (1)$$

or

$$e = \frac{V}{n} \frac{S}{[B\cdot]} \cdot \frac{[H\cdot]}{K} \quad . \quad . \quad . \quad (2)$$

As an example may be taken the Winkler titration of carbonic as a dibasic acid.

The end-point after neutralisation with sodium hydroxide is about 11·5 (see pp. 299, 300, Chap. VII.), which involves too high an hydroxyl error, $\frac{V}{n} \frac{K_w}{[H\cdot]}$.* In the presence

* It has been calculated by Bjerrum that even with a very small volume and using normal solutions the error is at least 1 per cent.

of $BaCl_2$ the end-point may be made about 9, which gives an hydroxyl error of 0·01 c.c. of 0·1 N. solution if the total volume is 100 (see p. 253).

At this $[H^{\cdot}]$ the acid error would be much higher (it is $\frac{[H^{\cdot}]}{K_2}$ or $10^{1\cdot22}$ times the $CO_3''$ present) were it not that $CO_3''$ is kept low by the slight solubility. If $BaCl_2$ is added in amount only just equivalent to the total carbonic acid (or the titration is carried out with $Ba[OH]_2$) the maximum value of $CO_3''$ is given by $\sqrt{S}$ above or $\sqrt{8\cdot1 \times 10^{-9}}$ (see Chap. VII., p. 321). On account of hydrolysis, however, $[Ba^{\cdot\cdot}]$ in such a solution will actually be greater and $(CO_3'']$ less than $9 \times 10^{-5}$. It is better, however, to increase $[Ba^{\cdot\cdot}]$ by addition of $BaCl_2$ in slight excess, the amount of which is given by equation (2) above. Thus if the error is to be 0·01 cc. of a 0·1 N. solution

$$[Ba''] \geqq \frac{V}{n} \times \frac{S}{0\cdot01} \times \frac{[H^{\cdot}]}{K_2} = \frac{100}{0\cdot1} \times \frac{10^{-8\cdot09}}{0\cdot01} \times \frac{10^{-9}}{10^{-10\cdot22}} = 10^{-1\cdot87},$$

or the solution should be made 0·0135 molar with respect to $BaCl_2$.

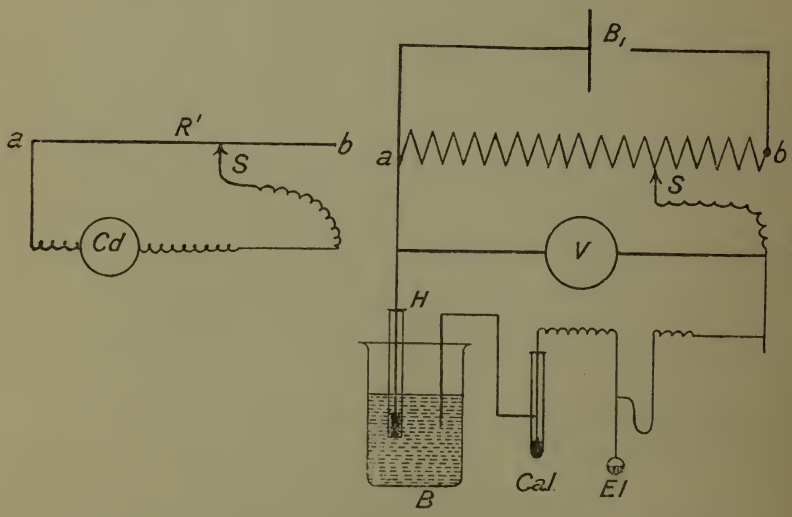
For further details of this titration Chap. VII., p. 320, should be consulted.

*Use of the Hydrogen Electrode in Titrations and in the Direct Determination of the $[H^{\cdot}]$ of Solutions.*

If the $[H^{\cdot}]$ of a solution is measured at intervals after the addition of successive quantities of alkali, the results will when plotted form a curve of neutralisation, and the amount of titrant corresponding to the known $[H^{\cdot}]$ of the end-point will be the titre of the solution. The curves of many acids and bases have been thus determined by Bottger, *Zeitsch. phys. Chem.*, 24, 253 (1897), and by Hildebrand,

*J. Amer. Chem. Soc.*, 35, 847 (1913). The other half electrode is usually one of the KCl calomel standards, and the diffusion potential is eliminated by the usual methods. The hydrogen electrode is conveniently of the dipping variety and is placed directly in the beaker of titrate. Suitable forms have been described by Bottger and Hildebrand.

An electrode which is strong and suitable for technical




work has been devised by Sand, *J. Soc. Chem. Ind.*, 30, 872 (1911).

The necessary electrical connections for this kind of work (without contact keys) are shown in the sketch. The slider S is adjusted on the rheostat R until the voltmeter V (in 0·01 volts) shows the potential which is required to exist between the hydrogen electrode H and the calomel electrode Cal at the end-point. The tapping key in this circuit is depressed at intervals during the titration until the electro-

meter El (or galvanometer) shows no deflection. If readings are required at various stages of the neutralisation the alteration in procedure is obvious. The rheostat R may, of course, be replaced by a straight wire potentiometer R′, the fall of potential along which is calibrated by a standard cell Cd in the usual manner. In this case the standard cell will usually be disconnected after it has been used to calibrate the bridge readings. The rise or fall of potential will become more marked at the end-point. From experimental results obtained in this manner the diagrams on pp. 234, 275, 282 have been reproduced by the kind permission of Professor Hildebrand.

While many of the disadvantages of the hydrogen electrode have been overcome by the appliances described, yet others remain which should be carefully noted. The hydrogen electrode is inapplicable when the gas in the presence of spongy platinum would reduce the acid or base, and also in other cases where the potential is ill defined for various reasons. Thus it cannot be used in the presence of ammonia or hydrogen sulphide.

On the other hand, the electrometric method is particularly valuable in the presence of proteins, which interfere more or less with the reliability of all indicators (see p. 210). Also in the titration of physiological solutions containing very small amounts of weak and very dilute electrolytes the [H·] change is so gradual, that region of maximum inflexion can only be obtained from a curve, since indicator changes are indefinite. The form of electrode vessel described by Walpole, *Biochem. J.*, VII. 4, 418 (1913), is particularly suitable for this purpose. The vessel is filled with hydrogen, and then liquid is drawn in by means of a plunger, the potential measurement is made, the liquid (which need only be about 3 c.c.) is expelled into the titration beaker again, and so on. The solution in the beaker is connected with

the saturated KCl calomel half electrode by means of a long tube tightly packed with cotton wool, which is soaked in the KCl solution. In the titration of liquids containing dissolved gases the type of vessel described on p. 43, Chap. I., should be used. An account of the technique of determining the neutralisation curve of $Na_2CO_3$ with HCl is taken from Walpole's paper, p. 425, referred to on p. 44.

"If the electrode vessel be tipped sideways when filling, the liquid drawn up may be made to enter the side capillary leaving a bubble of hydrogen. After closing the tap the apparatus may be taken in the hand, and by a slight movement at the wrist the bubble may be made to pass from one end of the vessel to the other as many times as are necessary to obtain equilibrium. Bringing the vessel into a vertical position again, the lower end is dipped below the surface of the fluid in the beaker, and the glass tube moved up or down through the rubber stopper until the platinum point just touches the surface of the column of fluid standing up in the electrode vessel. This may now be wiped dry externally, placed in the trough (thermostat), and a reading of the potential taken. . . . When small quantities only of carbon dioxide are present this value will be nearly correct. It may be checked by attaching a rubber tube to the tube at D (see p. 43, Chap. I.) and opening the tap gently. In this way fresh solution is drawn into B in place of the old solution which passes out through D without disturbing the hydrogen bubble. This fresh quantity of solution is now brought into equilibrium with the bubble of hydrogen as before. . . . It is essential that the platinum point shall only just touch the surface of the fluid when a reading is to be taken, otherwise equilibrium between the electrode and the solution, instead of taking only a minute or two, may take hours."

The results obtained must, of course, at higher pressures

of $CO_2$ be corrected for the decrease in the partial pressure of the hydrogen according to p. 51, Chap. I.

*The Hydrion Concentration and Titration of Tan Liquors and other Dark Solutions.*

The liquids used in the tanning industry owe a part of their value to the possession of a moderate and regulated hydrion concentration. A knowledge of this is therefore important and cannot certainly be obtained by the use of indicators, on account of the dark colour and also the presence of colloidal substances. The hydrogen electrode has therefore been applied by Sand, in conjunction with Wood and Law, *J. Soc. Chem. Ind.*, 30, 3 and 872 (1911), to the determination of the [H·] of the original solution and of the course of the titration.

The apparatus has been already partly described on p. 270.

Tables of the hydrogen potentials of various tan liquors are given. The [H·] values range from $4{\cdot}78 \times 10^{-4}$ (suspender) to $1{\cdot}4 \times 10^{-5}$ (first suspender). The potential of the normal hydrogen against the normal KCl calomel electrode was taken as + 0·283.

The reading was usually in the neighbourhood of 0·54 volt, that corresponding to absolute neutrality being 0·69 to 0·70 volt.

The acidity of tanning liquors is due to the presence of one or more of the following acids: acetic, formic, lactic, butyric (normal and iso-), carbonic and gallotannic.

The constants of most of these will be found in Chap. I. With regard to tannin, the E.M.F. of a freshly-made quebracho extract containing about 1 per cent. of tannin was about 0·54 volt, corresponding to an exponent of 4·53. The course of the neutralisation of fresh tan liquors is, as would be expected, very similar to that of an acid in low

concentration and having a constant lower than that of acetic acid. The curve of " ten-day liquor " was almost flat and more acid throughout. It appears, then, that the acidity of this is due to [H·] regulator, consisting probably of acids in higher concentration partly neutralised with calcium hydroxide. The characteristic forms of these curves will no doubt afford material assistance in the control and standardisation of tan liquors.

*The Titration of Magnesium and Calcium in Dolomite.*

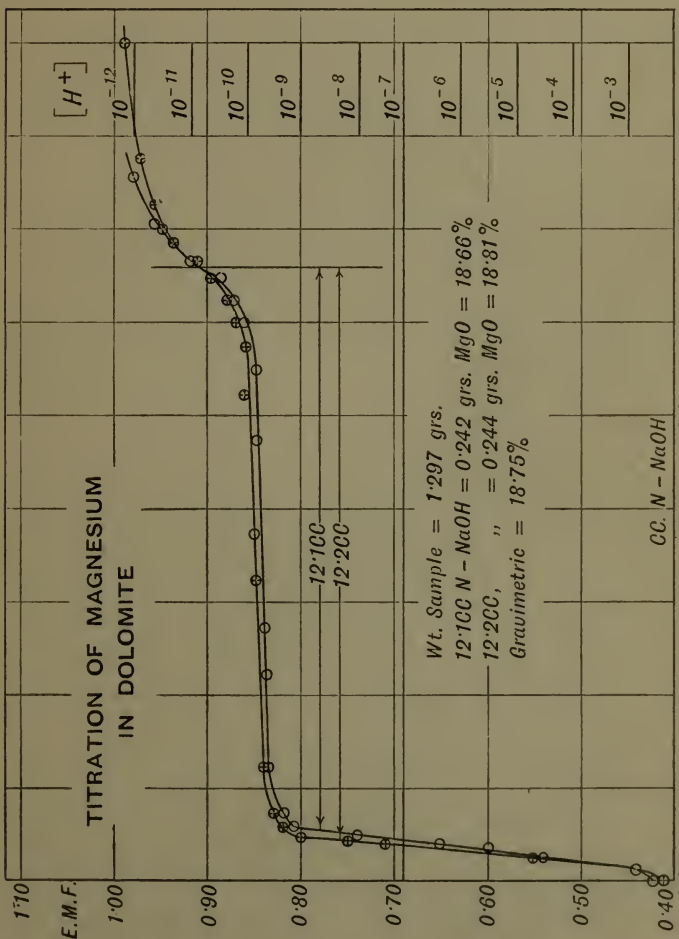
The well-known titration of carbonates which is carried out by dissolving them in excess of standard acid, boiling off the $CO_2$ and titrating back [H·] with methyl orange, gives the total alkali. If the addition of alkali is continued beyond the neutral point the hydroxides will be precipitated as soon as the [OH′] is greater than that which corresponds to the solubility product [B·] [OH′]. The possibility of titrating the magnesium and calcium separately may be shown on the electrometric neutralisation curve due to Hildebrand.

The steepest part of this curve corresponds to the neutralisation of the excess of standard acid. From about E = 0·82 the E.M.F. only increases slowly on the addition of alkali owing to the precipitation of $Mg(OH)_2$. When this is complete the curve rises again more sharply, the middle of the inflexion being at about E = 0·91, exponent = 9·2. The corresponding hydrogen exponent is 11, so that the titration could also be carried out with an indicator, although the [OH′] error would be rather high.

The experimental details are as follows:

The dolomite (about 0·4 gram.) is weighed into the flask, dissolved in dilute HCl, the $CO_2$ boiled out by a water pump vacuum, a trap being inserted to prevent loss of spray. The contents of the flask are then washed into a

beaker and titrated in the presence of methyl orange and of the dipping electrode, which has been previously saturated




with hydrogen. The E.M.F. is read when the solution is just yellow. The titration is then continued, occasional

readings of E.M.F. being taken until the final rise begins (at E = about 8·5), readings being then taken at each 0·2 c.c. until the end-point (see above) is reached.

The whole analysis occupies from 2 to $2\frac{1}{2}$ hours. The end-point can be obtained correctly to about 0·2 c.c. of normal alkali. The mean percentage of MgO in weights of sample ranging from 0·5 to 2 grams was found to be 20·6, the gravimetric result being 20·8.

# CHAPTER VII

## THE HYDRION EQUILIBRIA OF SOME IMPORTANT ACIDS

Boric, citric, phosphoric acids. Titration of boric and phosphoric in a mixture and in presence of magnesium or calcium salts. Carbonic acid. Solubility. Acidity due to atmospheric $CO_2$. Determination of the dissociation constants. The experimental and calculated neutralisation curves. The acidity of carbonate solutions in equilibrium with air. Tables. Loss and gain of $CO_2$ and the bicarbonate end-point. The alkalinity of blood serum. Very dilute carbonates. Alkalinity of hard waters and the carbonate equilibrium in nature. The titration of carbonic acid as bicarbonate and carbonate and that of total alkali in carbonates. Application of the theory of titration errors.

### *Boric Acid.*

As appears from the curve of standard solutions, Chap. V., p. 202, boric acid behaves as a weak monobasic acid. The constant of the dissociation as found by conductivity (Walker, *J. Chem. Soc.*, 77, 5 (1900) is $1{\cdot}7 \times 10^{-9}$ at 18°, a correction recently introduced by Arrhenius reduces this to $1{\cdot}06 \times 10^{-9}$. Hantzsch and Barth find $2{\cdot}3 \times 10^{-9}$ for the constant at 25°. A solution of the pure acid should therefore have a hydrion concentration greater than $1 \times 10^{-5}$, but a trace of alkali will greatly reduce it, the curve being steep in this part. Sorensen finds 6·55,* and Schmidt and Finger* 4·7. The former value was obtained by adding an equivalent of HCl to $NaH_2BO_3 + H_3BO_3$, and a very slight error in the amount added would easily account for this difference. The middle parts of the curve possess, however, a strongly balanced $[H^{\cdot}]$.

* *Biochem. Zeitsch.*, 21, 131 (1909); *J. Phys. Chem.*, 12, 413 (1908); 22, 352 (1910).

The data for the neutralisation curve are contained in Table, p. 279. The results of Sorensen (which apply to 0·2 molar acid) and those of Schmidt and Finger (0·25 molar) have been transformed in accordance with the mode of and presentation adopted in this book.

These results should agree with those deduced from the constant of Walker by the equation—

$$R = \frac{1 + \dfrac{K_W}{[H\cdot]a_B[NaH_2BO_3]}}{1 + \dfrac{[H\cdot]a_S}{K}}$$

(see p. 229, Chap. VI.), in which $a_S$ refers to the dissociation of $NaH_2BO_3$ and $a_B$ to that of NaOH. Since the solutions are not dilute the second term of the numerator is negligible in those which have not a high alkalinity. The results have been discussed in a note by the author, *Trans. Far. Soc.*, XI., i, May (1915).

The agreement is not good except just at the acid end of the curve, and the reason of this is to be sought in the formation of complexes in the partly neutralised solution. The existence of these is known from independent evidence. The value of the hydrogen exponent at 50 per cent. of neutralisation $NaH_2BO_3 + H_3BO_3$ is 9·25.

From this, taking $a_S = 0{\cdot}8$, a revised constant $K = 4{\cdot}5 \times 10^{-10}$ is obtained,* which gives the following in better agreement with the experimental results :—

| $-\log[H\cdot] =$ | 4·82 | 6·0 | 7·0 | 8·0 | 9·0 | 10·0 | 11·0 | 12·0 |
|---|---|---|---|---|---|---|---|---|
| $R =$ | 0·0 | $0{\cdot}0_35$ | 0·005 | 0·043 | 0·31 | 0·82 | 0·985 | 1·065 |

* Lundberg, *Zeitsch. phys. Chem.*, 69, 442 (1909), has calculated the [OH′] of borate solutions by the velocity of saponification of esters. The hydrolysis constant $\frac{[OH'][HBO_2]}{[BO_2']}$ at 25° was found to be $1{\cdot}9 \times 10^{-5}$ and from this the constant of boric acid in partly neutralised solutions ($K_W = 1{\cdot}21 \times 10^{-14}$) is $6{\cdot}4 \times 10^{-10}$.

The values of Sorensen have been used in drawing the curve of borate standards (end of book).

| Schmidt and Finger. 0·25 N. | | | Sorensen. 0·2 N.* | | |
|---|---|---|---|---|---|
| | C.c. NaOH to 10 boric. | −log [H·]. | | C.c. NaOH to 10 boric. | −log [H·]. |
| $H_3BO_3$ | 0 | 4·7 | | 0·0 | 6·55 |
| | 0·5 | 7·3 | | 0·48 | 7·6 |
| | 1·5 | 8·0 | | 0·91 | 7·94 |
| | 2·5 | 8·6 | | 1·30 | 8·14 |
| | 3·5 | 8·9 | | 1·67 | 8·29 |
| $NaH_2BO_3+H_3BO_3$ | 5·0 | 9·3 | | 2·30 | 8·51 |
| (borax) | 6·5 | 9·7 | | 2·85 | 8·68 |
| | 7·5 | 9·9 | | 3·33 | 8·80 |
| | 8·5 | 10·2 | | 3·75 | 8·91 |
| | 9·0 | 10·3 | | 4·11 | 9·01 |
| | 9·5 | 10·4 | | 4·45 | 9·09 |
| $NaH_2BO_3$ | 10·0 | 11·2 | | 4·75 | 9·17 |
| | 10·5 | 12·0 | $NaH_2BO_3$ | 5·00 | 9·24 |
| | 11·0 | 12·5 | $+H_3BO_3$ | 5·55 | 9·36 |
| | 12·0 | 12·7 | | 6·25 | 9·50 |
| | 13·0 | 13·0 | | 7·15 | 9·68 |
| | 15·0 | 13·3 | | 8·33 | 9·97 |
| | 17·0 | 13·4 | $NaH_2BO_3$ | 10·00 | 11·08 |
| $Na_2HBO_3$ | 20·0 | 13·5 | | 12·50 | 12·38 |
| | 23·0 | 13·6 | | | |
| | 25·0 | 13·7 | | | |
| | 27·0 | 13·5 | | | |
| $Na_3BO_3$ | 30·0 | 13·8 | | | |

* For the way in which these solutions were made, see p. 201.

*Titration of Borates.*

The ordinary titration of the total alkali in borax, etc., with N/2 HCl and a strong acid indicator is justified by the

curves. The calculated end-point being 4·8 (Schmidt and Finger 4·7), it would seem that methyl orange should not be turned to a full red, but that the first perceptible change towards orange should be noted as the end of the titration. Methyl red should give more accurate results, and para-nitrophenol, which is also used, is a suitable indicator, according to the tables. As the curve is steep here, however, any acid change point indicator will give fair results.

In the usual analytical procedure no attempt is made to titrate pure boric acid with alkali. The reason is evident from the flatness of the middle part of the curve at 9 to 10, which precludes a sharp titration with phenolphthalein. There is, however, a somewhat steeper part to the curve at $NaH_2BO_3$, although the OH′ error is here rather high. The experimental value of $-\log [H^{\cdot}]$ is 11·08 to 11·2 at $c = 0{\cdot}2$. According to Walker 0·1 $NaBO_2$ is hydrolysed to about 0·84 per cent., and therefore $-\log [H^{\cdot}]$ is 11·07. Salm calculates 10·85 at 25°. The effect of dilution on this hydrolysis may be expressed by the formula $[H^{\cdot}] = 3{\cdot}3 \times 10^{-12}\sqrt{\frac{1}{c}}$ at 18°, and this gives at c = 0·01 $-\log [H^{\cdot}] = 10{\cdot}5$. Thus at all ordinary concentrations an indicator would be required which changes at about 11. Of these indicators the author found tropaolin O the most suitable. Using about 0·5 c.c. of a 0·04 per cent. indicator, 0·2 molar boric acid and 0·5 N. alkali an accuracy of about 1 per cent. could be obtained (*Zeitsch. anorg. Chem.*, 83, 362 (1913).

In the titration as usually carried out glycerol or mannite is added.* These destroy the pink colour of the phenolphtha-

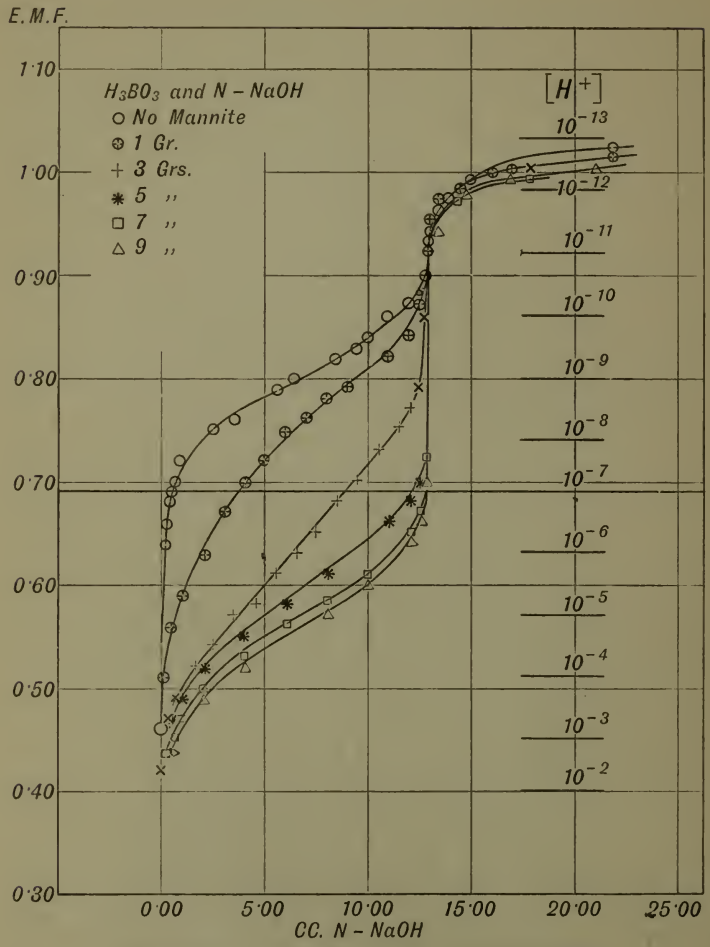
* Thomson, *J. Soc. Chem. Ind.*, 12, 433 (1893); Honig and Spitz, *Zeitsch. anal. Chem.*, 42, 120 (1903); Mandelbaum, *J. Soc. Chem. Ind.*, 28, 704 (1909): 29, 519 (1910); Jones, *Amer. J. Sci.*, 1909.

lein as it is produced, until finally with a sufficient addition of mannite, etc., and alkali (one equivalent) the colour persists. It has been proved by several methods that these additions raise the acidities throughout the titrations, and also at the end-point, bringing it within the range of phenolphthalein. Thus additions of mannite increase the conductivity of boric acids and borates to 50 or 100 times their original value and the dissociation constant calculated from $[H^{\cdot}]$ at $R = 0{\cdot}5$ rises to $1 \times 10^{-5}$ (Magnanini, *Zeitsch. phys. Chem.*, 6, 62 (1890); see also Auerbach, *Zeitsch. anorg. Chem.*, 37, 353 (1903)). The progressive increase

| Without Mannite. | | | With Mannite. | | |
|---|---|---|---|---|---|
| Per cent. neutralised. | Indicator. | $-\log [H^{\cdot}]$. | Per cent. neutralised. | Indicator. | $-\log [H^{\cdot}]$. |
| 0 | Lacmoid | 5 → 6·6 | | | |
| 1 | Lacmoid and P. nitrophenol | 6 → 7 | 0 | Methyl orange and methyl violet | 3 |
| 10 | Phenol-phthalein | 8 | 10 | Congo and lacmoid | 4 |
| 50 | Phenol-phthalein | 9·3 | 50 | P. nitrophenol | 5 |
| 90 | *a* naphthol benzoin | 10·3 | 90 | P. nitrophenol | 6 |

of the strength of boric acid on the addition of successive quantities has been strikingly shown by the titration curves of Hildebrand, p. 282.

The effect, which is probably due to the formation of a complex acid of higher ionisation constant, appears to be complete when mannite to the amount of about ten times




Electrometric Neutralisation Curve of Boric Acid.

the weight of the boric acid has been added. In the author's experience the end-point is the same, but requires a smaller addition of mannite if the solutions are saturated with NaCl.

The presence of carbonic or other weak acids falsifies the

titration of boric acid, and insoluble borates also introduce difficulties. By the method of Wherry and Chapin, *J. Amer. Chem. Soc.*, 30, 1687 (1908), the mineral or other sample to be analysed is fused with $Na_2CO_3$, acidified with 1 : 1 HCl, oxidised with $HNO_3$ and boiled under a reflux condenser after the addition of $CaCO_3$. The iron and aluminium precipitate is filtered and the solution boiled with a little more $CaCO_3$ in a filter pump vacuum until the temperature falls to 50°. The calcium bicarbonate is thereby decomposed and the boric acid free from carbonic is titrated in the filtered solution in the usual way.

Another method depends upon the formation of methyl borate from methyl alcohol in acidified borate solutions. The methyl borate is decomposed by water, and in absence of other volatile acids may be titrated with phenolphthalein after addition of glycerol or mannite.

The sample 0·3 to 0·5 gram. after alkali fusion, if necessary, is dissolved on the water bath in 1 : 1 HCl with addition of anhydrous $CaCl_2$ (1 gram. to 1 c.c. of solution). The distillation is carried out by passing the vapour of methyl alcohol through the solution on the water bath. The boric acid in the distillate is found approximately by titrating first with paranitrophenol and then with phenolphthalein, an amount of alkali is added equal to the difference in the titrations, and the methyl alcohol is distilled off. The volume of the liquid is then made up to 25 c.c., HCl 1 : 1 is added until the paranitrophenol is decolorised, then $CO_2$ is removed in the manner mentioned above and the boric acid titrated as usual, beginning at the point at which paranitrophenol is changed back to yellow.

### *Citric Acid.*

As is seen from Table, p. 21, Chap. I., citric is a medium strong acid, of which the first two constants are of the

same order as those of acetic acid. Hence an exceptionally long section of the curve, beginning with the pure acid, is only slightly inclined to the axis of abscissæ, and is therefore most suitable for the preparation of [H·] regulators of moderate acidity (see Chap. V.).

The whole curve of neutralisation has been determined by Enklaar (ref. on p. 235, Chap. VI.), using the electrometric method. In the diagram, p. 236, the abscissæ are equivalents of alkali × 100 to 1 mol of acid. If one equivalent of the acid is taken instead, the curve becomes not unlike that of a strong monohydrion acid, but is on a lower level of acidity.

*Neutralisation Values of $\frac{1}{6}$ Molar Citric Acid, 35 grams to the litre.*

R = equivalents NaOH to 100 mols of acid.

| | | | | |
|---|---|---|---|---|
| R = | 0·00 | 15·0 | 30·0 | 45·0 |
| − log [H·] = | 1·9540 | 2·3656 | 2·6828 | 2·9376 |
| R = | 60·0 | 75·0 | 90·0 | 105 |
| − log [H·] = | 3·2062 | 3·4420 | 3·6447 | 3·8232 |
| R = | 120 | 135 | 150 | 165 |
| − log [H·] = | 4·0416 | 4·2409 | 4·3761 | 4·5147 |
| R = | 180 | 195 | 210 | 225 |
| − log [H·] = | 4·7054 | 4·8943 | 5·0295 | 5·2131 |
| R = | 240 | 255 | 270 | 285 |
| − log [H·] = | 5·3484 | 5·5667 | 5·8180 | 6·1577 |
| R = | 295·7 | 296·3 | 297·5 | 297·8 |
| − log [H·] = | 7·0953 | 7·2896 | 7·7920 | 7·9220 |
| R = | 298·0 | 300 | 315 | 330 |
| − log [H·] = | 7·9983 | 11·2080 | 12·5373 | 12·7470 |

The dissociation constants were calculated by the author of this paper from the above results. The values of $K_1$

calculated from the equations of the first dissociation, are concordant up to 30 mols of NaOH to 100 of citric acid.

$K_1 = 0{\cdot}76 \times 10^{-3}$

$K_1 = 0{\cdot}83 \times 10^{-3}$ by conductivity at 25° (Noyes).

The second constant is then calculated, neglecting the third, and is found to be about 1 to 4 $\times$ $10^{-5}$. The want of constancy shows that the third constant is of nearly the same order and can therefore not be neglected even to a first approximation.

*Titration.*—The form of the curve shows that citric can only be titrated as a tri-hydrion acid. The phenolphthalein change-point (exact tint not important) corresponds to about a neutralisation of about 98 per cent. of the acid.

### *Phosphoric Acid.*

The neutralisation curve of $\frac{1}{15}$ molar $H_3PO_4$ from $NaH_2PO_4$ to $Na_2HPO_4$ is given by the measurements of Sorensen (Chap. V., p. 203 and chart).

For the $\frac{1}{10}$ molar acid from $NaH_2PO_4$ to $Na_3PO_4$ some results have been obtained by Salm, *Zeitsch. phys. Chem.*, 57, 492 (1907), and the author, *J. Chem. Soc.*, 99, 1224 (1911).

The former series are denoted by S, the latter by P. Solutions S were made from the crystallised mono-, di- and tri-sodium phosphate, solutions P chiefly from alkali and phosphoric acid.

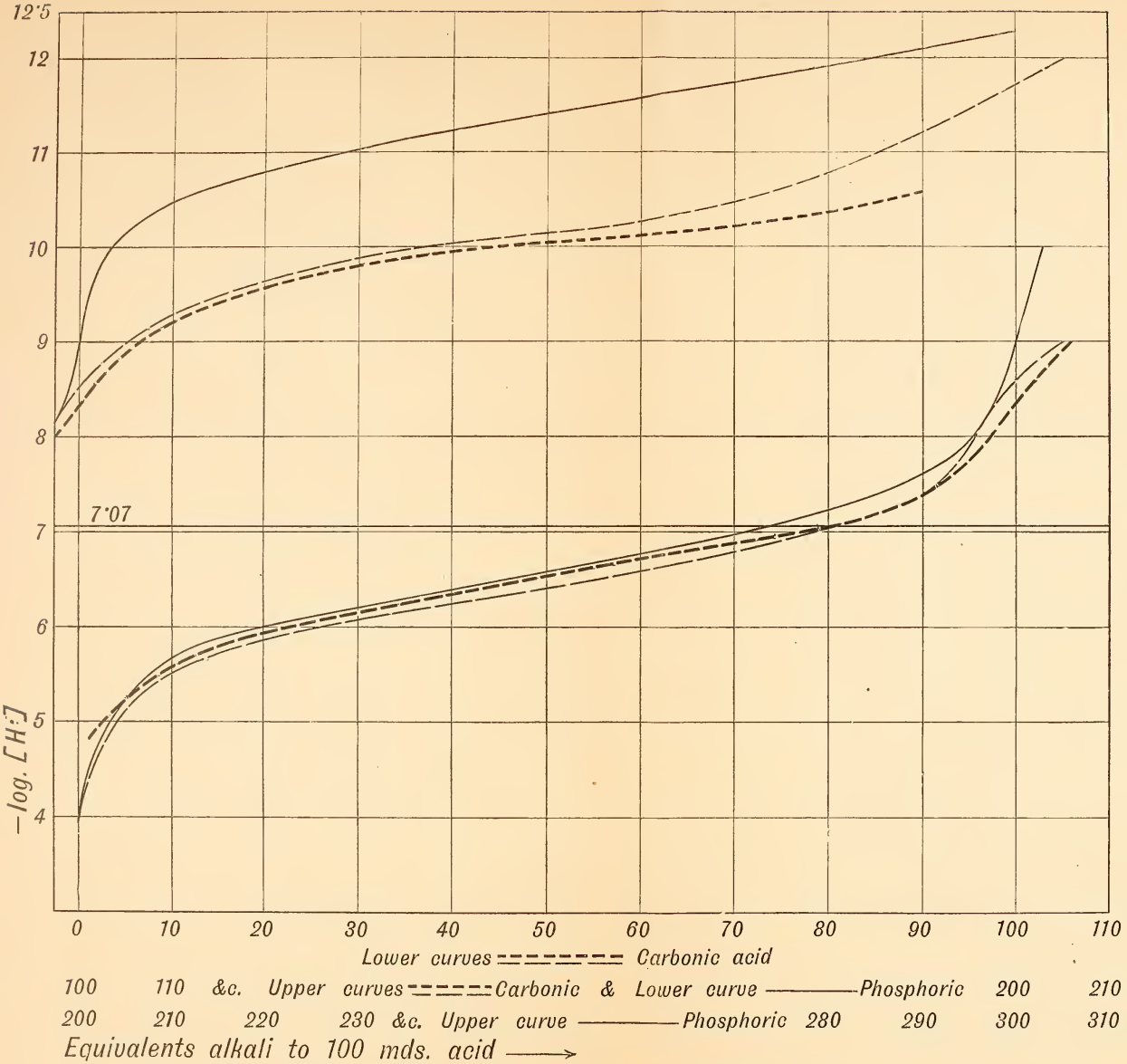
| | | | | |
|---|---|---|---|---|
| 100 R= | 100 ($NaH_2PO_4$) | | 106 | 110·5 |
| [H·] found= | $9{\cdot}3 \times 10^{-5}$ S | $1{\cdot}5 \times 10^{-4}$ P | — | $1{\cdot}7 \times 10^{-6}$ P. |
| [H·] calculated= | $1{\cdot}2 \times 10^{-4}$ | | $1{\cdot}0 \times 10^{-5}$ | — |
| 100 R= | 115 | | 120·5 | 144·5 |
| [H·] found= | $9{\cdot}7 \times 10^{-7}$ S | | — | $2{\cdot}6 \times 10^{-7}$ P |
| [H·] calculated= | — | | $1{\cdot}0 \times 10^{-6}$ | $3{\cdot}2 \times 10^{-7}$ |

| | | | |
|---|---|---|---|
| 100 R= | 155·0 | — | 172·0 |
| [H·] found= | $1{\cdot}5\times10^{-7}$ S | $2{\cdot}0\times10^{-7}$ P. | — |
| [H·] calculated= | — | — | $1{\cdot}0\times10^{-7}$ |
| 100 R= | 177 (neutral) | 176 | 195 |
| [H·] found= | — | $0{\cdot}76\times10^{-7}$ P | $1{\cdot}0\times10^{-8}$ S |
| [H·] calculated= | $0{\cdot}73\times10^{-7}$ | — | — |
| 100 R= | 196 | | |
| [H·] calculated= | $1{\cdot}0\times10^{-8}$ | | |

| | | | |
|---|---|---|---|
| 100 R= | 200 ($Na_2HPO_4$) | 200·4 | 203 |
| $-\log$ [H·] found= | $1{\cdot}3\times10^{-9}$ S<br>$1{\cdot}5\times10^{-9}$ P | — | $9{\cdot}8\times10^{-11}$ S |
| $-\log$ [H·] calculated= | $1{\cdot}0\times10^{-9}$ S | $1{\cdot}5\times10^{-10}$ | — |
| 100 R= | 205 | 214 | 216 |
| $-\log$ [H·] found= | $5{\cdot}9\times10^{-11}$ P | $1{\cdot}3\times10^{-11}$ S | $2{\cdot}0\times10^{-11}$ P |
| $-\log$ [H·] calculated= | — | — | — |
| 100 R= | 222 | 226 | 250 |
| $-\log$ [H·] found= | $1{\cdot}2\times10^{-11}$ P | — | $2{\cdot}9\times10^{-12}$ P |
| $-\log$ [H·] calculated= | — | $1{\cdot}0\times10^{-11}$ | $4{\cdot}0\times10^{-12}$ |
| 100 R= | 300 | | |
| $-\log$ [H·] found= | $4{\cdot}3\times10^{-13}$ S | $6{\cdot}8\times10^{-13}$ P | |
| $-\log$ [H·] calculated= | $5{\cdot}0\times10^{-13}$ | | |

These results can be expressed by equations containing the constants of the second and third dissociations. These constants as well as the degrees of ionisation of the sodium salts were determined by Abbott and Bray, *J. Amer. Chem. Soc.*, 31, 760 (1909).

$$\frac{[H\cdot][H_2PO_4']}{H_3PO_4} = K_1 = 1{\cdot}1\times10^{-2}$$




Neutralisation curves of 0·1 molar phosphoric acid (plain line).
" " 0·1 " carbonic " (broken line).
" " 0·001 " " " (dotted line).

$$\frac{[H^{\cdot}][HPO_4'']}{[H_2PO_4']} = K_2 = 1{\cdot}95 \times 10^{-7}$$
$$\frac{[H^{\cdot}][PO_4''']}{[HPO_4'']} = K_3 = 3{\cdot}6 \times 10^{-13}.$$

The experimental data were those of conductivity and distribution ratio (ammonium phosphates). The author has used the electrometric measurements referred to above to check the constants for $\frac{1}{10}$ molar acid. The value of $K_2$ in round numbers $2{\cdot}0 \times 10^{-7}$ was confirmed, but $K_3$ was found to be $3{\cdot}0 \times 10^{-12}$, instead of the value given above. These constants were used to calculate the R, $-\log [H^{\cdot}]$ values of the third line in the table which are marked as + on the curve. The points down to about $[H^{\cdot}] = 1 \times 10^{-11}$ may be obtained by the formula—

$$R = \frac{2 + \frac{0{\cdot}78[H^{\cdot}]}{K_2} + \frac{3{\cdot}6\ K_3}{[H^{\cdot}]}}{1 + \frac{0{\cdot}78[H^{\cdot}]}{K_2} + \frac{1{\cdot}2\ K_3}{[H^{\cdot}]}},$$

which contains the factors of incomplete ionisation, 77 per cent. for $NaH_2PO_4$ and 60 per cent. for $Na_2HPO_4$. For higher alkalinities and dilutions other formulae were employed, and the curve so calculated agreed with the experimental parts up to $R = 3$ ($Na_3PO_4$).

*Titration.*

The curves give information as to the best way of titrating this acid in steps, a procedure which was suggested by Thomson, *Chem. News*, 47, 123 (1883). The first hydrogen being that of a strong acid may be titrated with methyl orange. At the point $NaH_2PO_4$ of $\frac{1}{10}$ molar acid the exponent is 4. Sorensen finds 4·5 for $\frac{1}{15}$ molar acid. If methyl orange is used then, the colour at the end-point should be distinctly or completely yellow. A comparison

solution of citrate (3·3 HCl + 6·7 citrate) may be used. The titration of the second step with phenolphthalein is also sharp. Since $\frac{1}{10}$ molar $Na_2HPO_4$ gives an exponent of about 9, a little indicator may be used and the titration continued to a decided pink. Here, also, it is better to use a comparison solution, *e.g.*, borate and HCl (see p. 202, Chap. V.).

It may easily be shown that the error in titrating to $Na_3PO_4$ is so high as to make this titration useless.

The theory of Bjerrum may also be applied to the titration of phosphoric acid, the three K values of a given titration equivalent of the acid T being plotted on a diagram similar to that of p. 265, Chap. VI. The titration of the first H· requires the maximum possible concentration of $H_2PO_4'$ and the minimum of $H_3PO_4$ and $HPO_4''$. This maximum of primary dissociation is according to p. 238, Chap. VI., to be found at $[H\cdot] = \sqrt{K_1K_2}$. The best exponent is therefore $(1{\cdot}96 + 6{\cdot}7)/2 = 4{\cdot}33$.

In a diagram similar to that referred to above, this point may be found by drawing diagonals at 45° from $K_1$ (to left) and $K_2$ (to right). The ordinate of this point which gives the accuracy depends upon the ordinates at which $K_1$ and $K_2$ have been fixed, *i.e.*, the $T_1$ values. If it is assumed that the phosphoric acid is equivalent to 20 c.c. of the 0·1 N. alkali used, then the error due to—

$$H_3PO_4 \text{ is } -T_A\frac{[H\cdot]}{K_1} = -T_A\frac{10^{-4\cdot33}}{10^{-1\cdot96}} = -T_A\,10^{-2\cdot37}$$

$$= -\frac{T_A}{235},$$

or almost $\frac{1}{2}$ per cent. on the alkali used.

The error due to $HPO_4''$ is

$$+T_a\frac{K_2}{[H\cdot]} = +T_a\frac{10^{-6\cdot7}}{10^{-4\cdot33}} = +\frac{T_a}{235}.$$

These errors will not in general compensate one another for the reasons already given on p. 256, Chap. VI. Since the probable error is thus 0·09 c.c. on 20, there is no advantage in reducing the [H·] error below 0·05.

Therefore $10^{-4\cdot3}\frac{V}{n} < 0\cdot05$

and if $n = 0\cdot1\ V < 100$ c.c.

The total volume of the titrated solution may therefore have any value below 100 c.c.

In the titration of the second H· the correct end-point will be given by—

$$-\log [H\cdot] = \frac{6\cdot7 + 11\cdot52}{2} = 9\cdot11.$$

This corresponds to about the middle point of the visible change interval of phenolphthalein (see p. 157, Chap. IV.). The error due to $HPO_4'$ and that due to $PO_4'''$ will at this point be equal to one another and to

$$T\,\frac{10^{-9\cdot11}}{10^{-6\cdot7}} = T\,.\,10^{-2\cdot4} = \frac{T}{250}.$$

The accuracy is therefore 0·08 c.c. on 20, and if the OH′ error is to be below 0·05 c.c.

$$\frac{10^{-14}}{10^{-9\cdot11}}\frac{V}{n} < 0\cdot05$$

or if $n = 0\cdot1\ V < 390$ c.c.

The conclusion is that the error on the titration of each step is about ½ per cent., and the solutions may be fairly dilute.

*The Titration of Phosphoric and Boric Acids in presence of one another and of Salts of Mg and Ca.*

The special behaviour of boric acid with mannite enables

it to be titrated in the presence of acids which are stronger than boric without this addition. Biltz and Marcus* have attempted to titrate the phosphoric and leave the boric in the free state. They find that in the titration of pure phosphoric acid the first step with methyl orange requires a little more alkali than the second with phenolphthalein. Thus 5 c.c. of $\frac{1}{5}$ molar phosphoric acid requires (1) 10·5, (2) 9·5 c.c. of 0·1 N. NaOH, the total 20·0 being correct. The addition of boric acid makes the second step, and therefore the total phosphoric a little too high Thus 5 c.c. of 0·2 molar $H_3PO_4$ + 5 c.c. of 0·2 molar $H_3BO_3$ required.

| C.c. alkali with | 10·5 methyl orange | 10·3 phenolphthalein | 9·3 phenolphthalein with mannite. |
|---|---|---|---|

Some of the boric acid is neutralised at the $Na_2HPO_4$ change point, so that the titre of the boric acid, which should be obtained after the addition of mannite, appears too low.

The presence of ions which can form very slightly soluble precipitates with acids has the effect described under the Winkler titration of carbonic acid. The [H·] of salts of even very weak acids is thus brought up to the neutral point. The principle is valuable and capable of wide application. The question whether insoluble Mg and Ca borates or phosphates are formed has a particular interest, because these salts are often present in solutions of which the phosphoric or boric acid has to be determined. It has been found that the titration results of boric acid are not affected even by a large excess of these salts.

Phosphoric solutions are differently affected by Mg and Ca salts. The former, added either before or after the titration, cause the alkali required to be too high, the second hydrion

* *Zeitsch. anorg. Chem.*, 77. 131 (1912).

requiring an excess of alkali amounting to about 3 to 5 of the whole. At the end of the neutralisation a turbidity appears, and the precipitate was found to correspond very nearly in composition to $Mg_3(PO_4)_2$. Although, therefore, phosphoric can be approximately titrated as a di-hydrion acid in the presence of $MgCl_2$, a soluble $MgHPO_4$ being formed, yet a certain amount of this changes according to the equation—

$$4\ MgHPO_4 = Mg_3(PO_4)_2 + Mg(H_2PO_4)_2.$$

In the presence of Ca salts, however, the precipitation of the tribasic phosphate is complete or nearly so, and the acid can be titrated as a tri-hydrion (Bongartz, *Arch. d. Pharm.*, 222, 846 (1884)).

The $CaCl_2$ must, of course, be present in excess. Table I. shows the results of the titration of phosphoric acid and Table II. that of the mixture in the presence of calcium salts.

### *The Titration of $MgNH_4PO_4$.*

This precipitate is often estimated volumetrically after solution in standard acid. If the first $[H^{\cdot}]$ of the phosphoric acid is to be set free the best end-point is 4·33 (see p. 288, this chapter).

It is necessary that none of the possible precipitates should be formed. The solubility of $Mg(OH)_2$ requires that the exponent should not be greater than about 8. The $[H^{\cdot}]$ at which $MgNH_4PO_4$ will be precipitated may be calculated from the ionic equations. With decinormal solutions it is about 4·56 (Bjerrum). Hence the above value of 4·33 may safely be used. It is obtained on the alkaline side of the methyl orange interval and on the acid side of the cochineal or carminic acid (Hebebrand, *Zeitch. anal. Chem.*, 37, 217 (1898); Raschig, *Zeitch. angew. Chem.*, 18, 374 (1905)).

TABLE I.

| Ratio mols $P_2O_5/CaCl_2$. | 1/3. | 1/6. | 1/12. |
|---|---|---|---|
| C.c. phosphoric acid ... ... ... | 6·66 | 6·66 | 6·66 |
| C.c. $CaCl_2$ ... ... ... ... ... | 20 | 40 | 80 |
| C.c. NaOH methyl orange... ... ... | 14·5 | 14·6 | 14·6 |
| ,, ,, phenolphthalein ... ... | 24·7 | 24·9 | 25·3 |
| ,, ,, total ... ... ... ... | 39·2 | 39·5 | 39·9 |
| C.c. NaOH required for tri-basic acid ... | 40·0 | 40·0 | 40·0 |

TABLE II.

| Ratio mols $P_2O_5 : B_2O_3 : CaCl_2$. | 1 : 1 : 0·5. | 1 : 1 : 3. | 1 : 1 : 12. |
|---|---|---|---|
| C.c. phosphoric acid ... ... ... | 10 | 5 | 5 |
| C.c. boric acid ... ... ... ... | 10 | 5 | 5 |
| C.c. $CaCl_2$ ... ... ... ... ... | 5 | 15 | 60 |
| C.c. NaOH methyl orange... ... ... | 21·0 | 10·5 | 10·5 |
| ,, ,, phenolphthalein + mannite ... | 42·5 | 28·6 | 29·3 |
| ,, ,, total ... ... ... ... | 63·5 | 39·1 | 39·8 |
| ,, ,, calculated ... ... ... | 63·3 | 40·0 | 40·0 |

*Carbonic Acid.*

The equilibrium relations of carbonic acid are of peculiar theoretical interest on account of the participation of the gas phase, and of practical interest on account of the fact that they regulate some most important conditions of sub-aerial and sub-aqueous life, and also the formation and disappearance of carbonate deposits.

The following equations determine the values of $H^{\cdot}$, $OH'$ and the other ions in solutions of free carbonic acid or of carbonates :—

$$[H^{\cdot}]\,[HCO_3'] \rightleftarrows K_1\,[H_2CO_3] \quad . \quad (1)$$

$$[H^{\cdot}]\,[CO''_3] \rightleftarrows K_2\,[HCO_3'] \quad . \quad . \quad (2)$$

for the homogeneous equilibrium in solution and

$$[CO_2]\ \text{(dissolved)} \rightleftarrows K p_{CO_2}$$

for the equilibrium between the gas phase and the solution.

It is clear that the value of $K_1$ as usually determined is obtained by considering all undissociated $CO_2$ in solution as $H_2CO_3$. Thus $[H_2CO_3]$ above and in what follows means $H_2CO_3 + CO_2$ (dissolved). This apparent constant contains $K'_1$, the true constant $=$

$$\frac{[H^{\cdot}]\,[HCO_3']}{H_2CO_3}$$

together with that of the equilibrium

$$[H_2CO_3] = K_3[CO_2].$$

If the total carbonic acid concentration is C,

then $$C = [CO_2] + [H_2CO_3] + [HCO_3']$$

and $$C - [HCO_3'] = [H_2CO_3] + [CO_2]$$
$$= [CO_2]\,(1 + K_3)$$

and $$K_1'K_3 = \frac{[H\cdot]\,[HCO_3']}{[CO_2]}$$

$$\therefore \frac{[H\cdot]\,[HCO_3']}{C-[HCO_3']} = \frac{[H\cdot]\,[HCO_3']}{[H_2CO_3]+[CO_2]} = \frac{K_1'K_3}{1+K_3} = K_1 \text{ (observed).}$$

An estimate of the true strength of carbonic acid has been made by Thiel and Strohecker, *Ber.*, 47, 945 (1914). When an equivalent quantity of the acid solution is rapidly added to an alkaline solution containing an indicator the alkaline colour of the indicator persists for a longer time than when a mineral acid or acetic acid is neutralised. In the latter case the time required for complete neutralisation depends only on the time of mixing, which can with practice be reduced to 0·4 seconds. The greater slowness of the carbonic acid neutralisation is attributed to the delay due to the reaction

$$CO_2 + H_2O = H_2CO_3.$$

By using smaller and smaller quantities of alkali the time required was progressively shortened. It was estimated from these experiments that in a 0·00812 molar normal $H_2CO_3 + CO_2$ solution at 4° only 0·67 per cent. of the total concentration is actually carbonic acid, and therefore available for instantaneous neutralisation. The ionic concentration of this acid was now calculated in the usual way. The solution contained 0·608 per cent. of ions, the fraction of the true acid dissociated is therefore 0·91, and on referring the dilution to the true acid

$$V = \frac{123}{0{\cdot}0067} = 18{,}380,$$

the dissociation constant is $5{\cdot}0 \times 10^{-4}$, or more than double that of formic acid, as would be expected from the substitution of OH for H. The indicator used was

tetrachlorphenolphthalein, which was preferred, as the more intense colour allows smaller quantities to be used.

The apparent constant $K_1$ was determined by Walker and Cormack, *J. Chem. Soc.*, 77, 5 (1900) (see also Knox, *Wied. Ann.*, 54, 44 (1894)), by means of the electrical conductivity of solutions of carbonic acid. In such solutions practically only the first dissociation comes into consideration. The limiting conductivities of H· and $HCO'_3$ at infinite dilution were taken as 316 and 40·5. The mean value of $K_1$ from a dilution of 27·5 to one of 110 litres to the molecule is $3{\cdot}04 \times 10^{-7}$. From this calculations can be made of the acidity of carbonic acid in aqueous solution and in equilibrium with $CO_2$ of various pressures, if it is combined with the known coefficients of solubility of $CO_2$.

These are, at different temperatures and a pressure of 1 atmosphere, according to Bohr and Bock, *Ann. der phys. u. Chem.*, 62, 614 (1897)—

| $t°$ | 0 | 10 | 15 | 18 | 25 |
|---|---|---|---|---|---|
| C.c. $CO_2$ at N.T.P. in 1 c.c. of water = | 1·713 | 1·194 | 1·019 | 0·928 | 0·759 |
| $CO_2$ in grams per litre = | 3·347 | 2·319 | 1·971 | 1·789 | 1·459 |

Hence if K is the absorption coefficient, *e.g.*, at 18° c.c. CO, dissolved by 1 c.c. $= Kp_{CO_2}$

and $K = 0{\cdot}928$.

The acidity of such solutions may be calculated by Henry's law, *e.g.*, for water saturated at 18° and $\frac{1}{2}$ an atmosphere, $C = 40{\cdot}7/2 = 20{\cdot}3$ millimols.

$$[H\cdot] = \sqrt{K_1 C} = 7{\cdot}85 \times 10^{-5}.*$$

The amounts of $CO_2$ dissolved at low partial pressures of the gas may be expressed as c.c. of $CO_2$ at N.T.P., dissolved

* The coefficient of absorption $C/p$ increases at higher pressures.

by 1 litre of water when the gas has a partial pressure of $\frac{1}{10000}$ atmosphere.

| | | | | | |
|---|---|---|---|---|---|
| $t$ = | 0 | 4 | 8 | 12 | 16 |
| V = | 0·1713 | 0·1473 | 0·1283 | 0·1117 | 0·0987 |
| $t$ = | 20 | 24 | 28 | | |
| V = | 0·0877 | 0·0780 | 0·0700 | | |

Hence the amount of $CO_2$ dissolved from air containing 0·03 per cent. by volume when the barometer is normal and the temperature is 18° is 0·01263 millimol per litre.

The conductivity of water in equilibrium with atmospheric air and due to the $CO_2$ is as follows—

| $t$ | $\chi$ in mhos. |
|---|---|
| 18 | $0{\cdot}64 \times 10^{-6}$ (Walker, p. 295). |
| 18° | $0{\cdot}875$ to $1{\cdot}195 \times 10^{-6}$ (Kohlrausch and Maltby).* |
| 25 | $0{\cdot}7 \times 10^{-6}$ (Kendall, *Phil. Mag.* [6] 23, 958). |

The second constant of carbonic acid may be obtained from the alkalinities observed in given mixtures of carbonate and bicarbonate solutions. From the [OH′] obtained by Shields, *Zeitsch. phys. Chem.*, 12, 175 (1893), using the velocity of saponification, Bodlander calculates that $K_2 = 1{\cdot}3 \times 10^{-11}$. From the amounts of $NaHCO_3$ and $Na_2CO_3$ in equilibrium with a fixed partial pressure of $CO_2$, McCoy (ref. p. 301) finds $K_2 = 6{\cdot}0 \times 10^{-11}$.

From Walker's result and ionic mobilities the degree of dissociation works out at 0·16, and therefore $[H^{\cdot}] = 2{\cdot}0 \times 10^{-6}$.

Auerbach and Pick, *Arb. Kais. Gesundheitsamt*, 38, 4, p. 562 (1912), have made a series of colorimetric (and in part electrometric) measurements of the alkalinity of carbonate and bicarbonate solutions, and have also carried out a critical survey of previous work. These authors first

* *Wiss. Abh. d. phys. tech. Reichsanstalt*, 3, 192 (1900).

arrive at a quartic equation connecting $[H\cdot]$, $K_1$, $K_2$ and the concentrations of carbonate and bicarbonate. By neglecting small products of a lower order and ignoring as a first approximation the incompleteness of the dissociation of salts, etc., a simplified form is obtained—

$$K_2 = \frac{[H\cdot]\,[Na_2CO_3]}{[NaHCO_3]} + \frac{[H\cdot]^2\,[NaHCO_3] + 2[Na_2CO_3]}{[NaHCO_3]K_1} \quad . \quad (1)$$

For a solution containing only bicarbonate this becomes

$$K_2 = \frac{[H\cdot]^2}{K_1} \text{ or } [H\cdot] = \sqrt{K_1 K_2} \quad . \quad . \quad (2)$$

$$\text{or } [OH'] = \frac{K_W}{\sqrt{K_1 K_2}}$$

If a mixture contains $NaHCO_3$ and $Na_2CO_3$, both in moderate concentration, the total amounts of these will not be materially affected by any displacement of equilibrium which may occur (since $[H\cdot]$ and $[OH']$ are never very large).

$$\text{Then } \frac{[HCO_3']}{[CO_3'']} = \frac{[NaHCO_3]}{[Na_2CO_3]} \text{ and } K_2 = \frac{[H\cdot]\,[NaHCO_3]}{[Na_2CO_3]} \quad . \quad (3)$$

If the solution contains chiefly $Na_2CO_3$ so that $[H\cdot] \leq 1 \times 10^{-10}$, then the original quartic equation becomes

$$K_2 = \frac{[H\cdot]^2[Na_2CO_3] - [H\cdot]K_W}{[H\cdot]\,[NaHCO_3] + K_W}, \quad . \quad . \quad (4)$$

or if carbonate only was taken—

$$K_2 = \frac{[H\cdot]^2[Na_2CO_3]}{K_W} - [H\cdot] = \frac{[Na_2CO_3]K_W}{[OH']^2} - \frac{K_W}{[OH']} \quad (5)$$

These equations serve to determine $K_2$, as the right hand sides contain experimental quantities. The equations of

McCoy (ref. p. 311) depending on the heterogeneous equilibrium may also be employed.

If the $CO_2$ pressure is kept constant $= p$ and $x =$ gram mols of $NaHCO_3$, $1 - x$ the mols of $Na_2CO_3$, and $c$ the total concentration, then—

$$\text{Constant (K)} = \frac{2x^2c}{0{\cdot}0338\,p\,[1-x]} = \frac{K_1}{K_2} \text{ at } 25° \quad . \quad (6)$$

The values of $K_2$ obtained by all these equations did not agree together completely, but when corrections were introduced for the incomplete dissociation of the bicarbonate, carbonate and hydroxide, the results of Auerbach and Pick all lay between $K_2 = 5{\cdot}5$ and $6{\cdot}0 \times 10^{-11}$. The final corrected values from the results of different experimenters were—

| Experimenter. | Shields. | Kœlichen.* | McCoy. | Auerbach and Pick. |
|---|---|---|---|---|
| $t$ | 24·2° | 25·2° | 25·0° | 18·0° |
| $10^{11}K_2$ | 6·4 | 6·6 | 6·0 | 6·0 |

In the case of pure bicarbonate, equation (2), p. 297, shows that in all moderately concentrated solutions the alkalinity is independent of the total concentration.

At 18° $[OH'] = 0{\cdot}15 \times 10^{-5}$ $[H\cdot] = 4{\cdot}3 \times 10^{-9}$
At 25° $[OH'] = 0{\cdot}25 \times 10^{-5}$ $[H\cdot] = 4{\cdot}5 \times 10^{-9}$

or the alkalinity is equivalent to about 0·02 millimol of hydroxylion per litre.

The results of Auerbach for the alkalinity of solutions intermediate between $NaHCO_3$ and $Na_2CO_3$ are given in the two following tables. In Table I. all solutions are 0·2 molar with respect to total $H_2CO_3$, in Table II. they are 0·1 normal with respect to total NaOH.

* *Zeitsch. phys. Chem.*, 33,172 (1900). The [OH'] was determined by its effect upon the rate of decomposition of diacetone alcohol into acetone.

TABLE I.

Alkalinities of $Na_2CO_3$ and $NaHCO_3$ (Auerbach and Pick).

| Mols per litre. | | Ratio. | | [H·] calculated. | |
|---|---|---|---|---|---|
| $NaHCO_3$ | $Na_2CO_3$ | $NaOH/H_2CO_3$ | [H·] | [OH′] | $-\log[H\cdot]$ |
| 0·20 | 0·00 | 1·00 | $4{\cdot}45\times10^{-9}$ | $1{\cdot}45\times10^{-6}$ | 8·35 |
| 0·19 | 0·01 | 1·05 | $1{\cdot}25\times10^{-9}$ | $5{\cdot}10\times10^{-6}$ | 8·90 |
| 0·18 | 0·02 | 1·10 | $7{\cdot}10\times10^{-10}$ | 9·00 | 9·15 |
| 0·16 | 0·04 | 1·20 | $3{\cdot}55\times10^{-10}$ | $1{\cdot}80\times10^{-5}$ | 9·45 |
| 0·14 | 0·06 | 1·30 | 2·25 | 2·85 | 9·65 |
| 0·12 | 0·08 | 1·40 | 1·10 | 5·70 | 9·96 |
| 0·10 | 0·10 | 1·50 | $7{\cdot}95\times10^{-11}$ | 8·05 | 10·10 |
| 0·08 | 0·12 | 1·60 | $4{\cdot}45\times10^{-11}$ | $1{\cdot}45\times10^{-4}$ | 10·35 |
| 0·06 | 0·14 | 1·70 | $3{\cdot}55\times10^{-11}$ | 1·80 | 10·45 |
| 0·04 | 0·16 | 1·80 | $2{\cdot}25\times10^{-11}$ | 2·85 | 10·65 |
| 0·02 | 0·18 | 1·90 | *$1{\cdot}00\times10^{-11}$ | 6·40 | 11·00 |
| 0·0 | 0·20 | 2·00 | †$1{\cdot}60\times10^{-12}$ | $4{\cdot}00\times10^{-3}$ | 11·80 |
| | | | *$2{\cdot}6\times10^{-12}$ | $2{\cdot}45\times10^{-3}$ | 11·59 |

* Colorimetric. † Electrometric.

TABLE II.

| Mols per litre. | | Total $[H_2CO_3]$ | Ratio $\frac{[NaOH]}{[H_2CO_3]}$ | [H·] | [OH′] | $-\log[H\cdot]$ |
|---|---|---|---|---|---|---|
| $NaHCO_3$ | $Na_2CO_3$ | | | | | |
| 0·10 | 0·00 | 0·10 | 1·00 | $4{\cdot}45\times10^{-9}$ | $1{\cdot}45\times10^{-6}$ | 8·35 |
| 0·09 | 0·005 | 0·095 | 1·05 | $1{\cdot}05\times10^{-9}$ | $6{\cdot}10\times10^{-6}$ | 8·98 |
| 0·08 | 0·010 | 0·090 | 1·12 | $5{\cdot}00\times10^{-10}$ | $1{\cdot}30\times10^{-5}$ | 9·30 |
| 0·07 | 0·015 | 0·085 | 1·175 | $3{\cdot}15\times10^{-10}$ | $2{\cdot}05\times10^{-5}$ | 9·50 |
| 0·06 | 0·020 | 0·080 | 1·25 | $2{\cdot}5\times10^{-10}$ | $2{\cdot}55\times10^{-5}$ | 9·60 |
| 0·05 | 0·025 | 0·075 | 1·33 | $1{\cdot}35\times10^{-10}$ | $4{\cdot}75\times10^{-5}$ | 9·87 |
| 0·04 | 0·03 | 0·07 | 1·43 | $8{\cdot}9\times10^{-11}$ | $7{\cdot}20\times10^{-4}$ | 10·05 |
| 0·03 | 0·035 | 0·065 | 1·54 | $5{\cdot}85\times10^{-11}$ | $1{\cdot}10\times10^{-4}$ | 10·23 |
| 0·02 | 0·040 | 0·060 | 1·67 | $4{\cdot}45\times10^{-11}$ | $1{\cdot}45\times10^{-4}$ | 10·35 |
| 0·01 | 0·045 | 0·055 | 1·82 | $2{\cdot}00\times10^{-11}$ | $3{\cdot}20\times10^{-4}$ | 10·7 |
| 0·00 | 0·05 | 0·050 | 2·00 | $3{\cdot}90\times10^{-12}$ | $1{\cdot}65\times10^{-3}$ | 11·41 |

For these moderately concentrated carbonate solutions the ratio R at a given [H·] may be obtained from equations (1*a*) or (1*b*) (Chap. VI., pp. 239, 240) if $NaHCO_3$, etc., are written for NaHA, etc.

The equation on p. 239, Chap. VI., may also be used in the middle part of the neutralisation curve, but when the alkalinity is higher (in solutions near $Na_2CO_3$) the latter simplified form does not give correct results. Thus at R = 2, $-\log [H\cdot] = 11{\cdot}7$ from formula (1*b*), and 12·3 from the approximate formula.*

The smoothed curve expressing all these results is given on p. 287.

The third terms of both numerator and denominator in the equation are negligible between $[H\cdot] = 1 \times 10^{-9}$ and $[H\cdot] = 1 \times 10^{-10}$.

TABLE III.

The calculated neutralisation curve of 0·1 molar $H_2CO_3$:

| | | | | |
|---|---|---|---|---|
| R = | 0·0 | 0·037 | 0·27 | 0·66 |
| $-\log [H\cdot]$ = | 3·75 | 5·00 | 6·00 | 6·70 |
| R = | 0·79 | 0·89 | 0·96 | 1·05 |
| $-\log [H\cdot]$ = | 7·00 | 7·30 | 8·00 | 9·00 |
| R = | 1·16 | 1·375 | 1·86 | 1·97 |
| $-\log [H\cdot]$ = | 9·50 | 10·00 | 11·00 | 11·50 |
| R = | 2·055 | 2·135 | | |
| $-\log [H.]$ = | 12·00 | 12·30 | | |

*Acidity of Carbonate Solutions in Equilibrium with the Air.*

If a solution of alkali is brought into equilibrium with $CO_2$ of any fixed partial pressure, then the concentration of $H_2CO_3$, and therefore of all the molecular species in equilibrium with it directly or indirectly, is also fixed. Therefore

* The values assumed for the dissociations of salts, etc., are $\alpha_1 = \alpha_2 = 0{\cdot}8$ $\alpha_3$ [NaOH] = 0·9.

for one total concentration of alkali there is one and only one total concentration of $CO_2$, and therefore only one alkalinity. Equilibrium appears to be only slowly attained in dilute solutions (see Walker and Kay, p. 313 this chapter), more quickly, however, in moderately concentrations solutions such as those investigated by McCoy, *Amer. Chem. J.*, 29, 437 (1903). A bicarbonate solution will lose $CO_2$ to the air, a carbonate will gain it until a certain definite ratio is established between alkali and total $CO_2$. In the experiments which proved these statements atmospheric air containing different amounts of $CO_2$ was drawn through a 0·1 N. solution of $NaHCO_3$. The amount of bicarbonate left was determined by the Winkler method; the solution was treated with $BaCl_2$ and a known excess of standard $Ba(OH)_2$. The amount of the latter used up corresponds to the bicarbonate present—

$$NaHCO_3 + Ba(OH)_2 = BaCO_3 + NaOH + H_2O.$$

At the beginning 95 per cent. of the Na was present as $NaHCO_3$, at equilibrium (in a little more than an hour) 40 per cent. The ratio R at this concentration is 1·43 and the value of $[H^{\cdot}]$ from the curve is $7{\cdot}94 \times 10^{-11}$. Such a solution therefore gives a full red with phenolphthalein.

The value of $[H^{\cdot}]$ enables a comparison to be made between the value of $H_2CO_3$ derived from McCoy's data with that which is required by the equilibrium between gaseous and dissolved $CO_2$.

For the former

$$[H_2CO_3] = \frac{[H^{\cdot}] \times [HCO'_3]}{K_1}$$

$$= \frac{7{\cdot}94 \times 10^{-11} \times 0{\cdot}4 \times 0{\cdot}8 \times 0{\cdot}1}{3{\cdot}04 \times 10^{-7}}$$

$$= 2{\cdot}55 \times 10^{-5}.$$

For the latter $H_2CO_3 = \frac{0{\cdot}076 \times 3}{22{,}300} = 1{\cdot}02 \times 10^{-5}$.

The number of mols of bicarbonate $Cx$ and of carbonate $C(1-x)$ in a solution of total concentration C is given by the equation

$$\frac{2x^2C}{0{\cdot}0338p\,(1-x)} = K = 5{,}290.$$

The constant is the average of the experimental values of the most dilute of the solutions investigated in Table I.

If the ionisations were complete, the constant K would be identical with

$$\frac{[HCO_3']^2}{[CO_3''][H_2CO_3]} = \frac{K_1}{K_2} = 5{,}070,$$

or using the value of $K_2(= 5{\cdot}5 \times 10^{-11})$ attributed by McCoy to more dilute solutions

$$\frac{K_1}{K_2} = 5{,}530.$$

It is evident from the tables below that, as would be expected, the more concentrated is the solution the further is K removed from the theoretical value at complete ionisation.

In calculating the average value of K from Table I. extra weight has been given to the results between 75 and 85 per cent. of $NaHCO_3$, as the accuracy of the analytical method employed is here at its greatest.

The amounts of Na present as $NaHCO_3$ and $Na_2CO_3$ may be found in any given solution of known alkali concentration in equilibrium with the air by means of the equation

$$\frac{x^2}{1-x} = \frac{K \times 0{\cdot}0338 \times 0{\cdot}0003 \times h}{2 \times 760 \times C}$$

In which $h$ = the barometic height in mm. Hg

$0{\cdot}0003$ = average pressure of the $CO_2$ of the air (in atmospheres)

C = concentration of the alkali

K = the value of the constant at the given con-

centration. This may be obtained by interpolation from the Tables I., II., III., and the summary Table IV.

TABLE I.

0·1 N. Alkali.

| Per cent. $NaHCO_3$ corrected for dissolved $CO_2$. | $100pCO_2$ in atmospheres. | $K \times 10^{-2}$ |
|---|---|---|
| 68·2 | 0·161 | 53·2 |
| 69·0 | 0·159 | 57·0 |
| 76·0 | 0·259 | 54·6 |
| 77·5 | 0·294 | 53·6 |
| 78·1 | 0·322 | 51·0 |
| 81·8 | 0·404 | 53·6 |
| 95·1 | 2·23 | 49·0 |
| 98·5 | 7·49 | 51·0 Mean K=5,290 |

TABLE II.

0·3 N. Alkali.

| Per cent. $NaHCO_3$ corrected for dissolved $CO_2$. | $100pCO_2$ in atmospheres. | $K \times 10^{-2}$ |
|---|---|---|
| 57·9 | 0·319 | 44·6 |
| 67·9 | 0·583 | 43·8 |
| 76·9 | 1·044 | 43·6 |
| 85·2 | 1·07 | 44·4 |
| 88·8 | 2·76 | 45·4 |
| 92·6 | 4·51 | 45·8 Mean K=4,460 |

TABLE III.

1·0 N. Alkali.

| Per cent. $NaHCO_3$ corrected for dissolved $CO_2$. | $100pCO_2$ in atmospheres. | $K \times 10^{-2}$. |
|---|---|---|
| 75·8 | 4·36 | 32·4 |
| 81·0 | 6·24 | 32·8 |
| 86·0 | 10·21 | 30·6 |
| 90·2 | 16·82 | 29·2 Mean K=3,120 |

TABLE IV.

| Total alkali equivalents. | $x$ = per cent. alkali as $NaHCO_3$. | $K \times 10^{-2}$. |
|---|---|---|
| 0·0044 | 87 | 53 |
| 0·0143 | 72 | 53 |
| 0·0562 | 49 | 53 |
| 0·2248 | 28 | 48 |
| 0·8847 | 13 | 33 |

The acidity of all these solutions might be obtained from equations (Chap. VI., pp. 239, 240) if a sufficient independent knowledge was available of the salt ionisations $a$, etc., at higher concentrations. As the total amount of NaOH in solution increases so does the alkalinity of solutions in equilibrium with the air. These mixtures might well be used as standard [H·] regulators, especially for finding the alkalinity of unknown solutions of serum, etc., containing carbonate.

*The $CO_2$ Pressure and Alkalinity of Bicarbonate Solutions.*

If a pure bicarbonate solution is made up without escape of $CO_2$, then the pressure of the latter and the alkalinity are both perfectly definite. A certain amount of $Na_2CO_3$ will be formed by hydrolysis.

$$2NaHCO_3 = Na_2CO_3 + H_2CO_3.$$

Suppose that in 0·1 N. $NaHCO_3$ there are $x$ mols of $NaHCO_3$ left and consequently $\frac{1-x}{2}$ each of $H_2CO_3 + Na_2CO_3$ are formed.

Then from p. 302 $$\frac{4x^2}{(1-x)^2} = 5{,}290$$

$$\therefore x = 0{\cdot}9732 \text{ and } 1 - x = 0{\cdot}0268$$

and $$H_2CO_3 = \frac{1-x}{2\times 10} = 0{\cdot}00134.$$

$$\text{Hence at } 25^\circ \; p_{CO_2} = \frac{0{\cdot}00134}{0{\cdot}0338} = 0{\cdot}0396 \text{ atm.}$$

Such a solution tends therefore to lose $CO_2$ until the pressure falls to about 0·0003 atmosphere.

The alkalinity may be calculated by means of the hydrolysis equation on p. 30, Chap. I. $K_h = \frac{K_w}{K_1} = 3{\cdot}95\times 10^{-8}$ at 25°.

In the above solution $[H_2CO_3]=0{\cdot}00134$ $[NaHCO_3]=0{\cdot}097$

and $$3{\cdot}95\times 10^{-8} = \frac{[NaOH]\,[H_2CO_3]}{[NaHCO_3]}$$

$\therefore [NaOH] = 2{\cdot}9\times 10^{-6}$, and assuming complete dissociation $[H^\cdot] = 4{\cdot}14\times 10^{-9}$.

The slightly higher result of Auerbach in Table II., p. 299, is probably a measure of the incompleteness of the dissociation of the NaOH. A solution of bicarbonate made up 0·1 N. in a closed vessel is therefore just within the range

of phenolphthalein. In contact with the air, however, it will gradually lose $CO_2$. At equilibrium, by interpolation from Table 1. on p. 303 it may be found that the per cent. of Na present as $NaHCO_3$ is 35. The alkalinity will rise accordingly, and since the neutralisation ratio R is now 1·5, — log [H·] from the curve on p. 287 will be 10·2, at which point a little phenolphthalein is turned a full red. These circumstances probably account for some of the disagreement as to the true end-point of bicarbonate. For although the alkalinity of bicarbonate solutions is, according to p. 287, only slightly dependent upon the original concentration, yet that of original bicarbonate solutions subsequently brought into equilibrium with the air is highly dependent upon the original concentration, because the ratio of alkali to acid which gives a fixed pressure of $CO_2$ varies rapidly with the concentration.

The relations between $CO_2$ pressure, total alkali dissolved and alkalinity, or [OH′], which are of fundamental importance in the solution and precipitation of carbonate minerals and in the aeration of the blood, may be elucidated by the methods outlined above. As an example will be taken the treatment of the latter problem.

*Carbon Dioxide and the Alkalinity of Blood.*

The dissolved salts of the blood serum which are capable of producing a balanced hydrion concentration are sodium bicarbonate and in much smaller amount primary and secondary sodium phosphate. The value of [H·] is mainly controlled by the ratio of alkali to carbonic acid; and the latter in its turn is being continually altered by the supply of $CO_2$ produced in the processes of the cells and by the loss of the gas to the air in the lungs.

The concentration and pressure of $CO_2$ is therefore greater in venous than in arterial blood, but is always such

that blood is alkaline (see Table, p. 308, below). The [OH'] can be found only indirectly by analysis—*i.e.*, if both the alkali and also the amount of carbonic acid is known, the [H·] can of course be calculated from the preceding equations and curves. On an average a litre of the serum contains 0·12 mol of $NaHCO_3$ and 0·01 mol of $H_2CO_3$. The ratio R is thus 0·92, and from the curve on p. 287 the value of $-\log [H\cdot]$ is 7·5, $[H\cdot] = 3 \times 10^{-8}$.

The [H·] of blood serum has also been determined with the aid of indicators by Friedenthal, *Zeitsch. allgem. Physiol.*, I., 56 (1901), and by many other physiological chemists since. It is alkaline to litmus, but not so to phenolphthalein. Therefore [H·] lies between $1 \times 10^{-7}$ and $1 \times 10^{-8}$.

The attempt to apply the hydrogen electrode to confirm these results met with considerable experimental difficulties. The quantities of liquid available are often but small; they give rise to foam bubbles when treated with a current of gas, and also lose some of their $CO_2$, becoming more alkaline. The names of Benedict, Farkas, Hasselbalch, Hober, Michaelis, Sorensen, Szili, and Walpole are prominent amongst those who have perfected the electrometric measurements of physiological liquids.

The E.M.F. of the hydrogen electrode in serum which is in equilibrium with the $CO_2$ pressure actually existing in the living animal has been accurately determined by Hasselbalch with the results given (38° C.):—

| | $-\log [H\cdot]$. | $[H\cdot]$. | $p_{CO_2}$ (in atmospheres) |
|---|---|---|---|
| Arterial | 7·45 | $3{\cdot}5 \times 10^{-8}$ | 0·0395 |
| Venous | 7·31 | $4{\cdot}9 \times 10^{-8}$ | 0·0658 |

Michaelis finds for venous blood at 18°—

7·56 $2{\cdot}75 \times 10^{-8}$.

The difference of 0·21 in the hydrogen exponent is that which is regularly found between measurements of the same solution at 18° and 38°.

The influence of a much greater alteration of $p_{CO_2}$ than that which is normally found has been investigated by Hober, *Pfluger's Archiv.*, 81, 522 (1900); 99, 572 (1903).

The E.M.F's. were found by means of hydrogen containing the equilibrium pressure of $CO_2$, and had therefore to be corrected according to p. 51, Chap. I.:—

| Per cent. $CO_2$ in $H_2$. | $[H^{\cdot}] \times 10^7$. | Per cent. $CO_2$ in $H_2$. | $[H^{\cdot}] \times 10^7$. |
|---|---|---|---|
| 0 | 0·012—0·028 | 6·51 | 0·79 |
| 1·6 | 0·31 | 9·19 | 0·89 |
| 2·44 | 0·47 | 9·95 | 0·74 |
| 3·18 | 0·37 | 15·50 | 0·94 |
| 3·81 | 0·34 | 26·35 | 1·55 |
| 4·15 | 0·49 | 29·05 | 2·37 |
| 4·26 | 0·58 | 57·86 | 2·98 |

The irregular fluctuations must be due to experimental errors. On the whole it appears that the $[H^{\cdot}]$ of blood is relatively insensitive to variations of $CO_2$ between 1·6 and 4·0 per cent. The fine regulation of the difference of $[H^{\cdot}]$ between venous and arterial blood can only be detected by great care in producing uniform experimental conditions. The means which the living animal possesses of regulating the $[H^{\cdot}]$ is not only the aeration in the lungs, but also the supply of $Na_2HPO_4$ and $NaH_2PO_4$ in varying proportions by the kidneys.

The disturbance of $[H^{\cdot}]$ caused by the addition of strong acids and bases can also be calculated. It is greater for equivalent amounts of the latter than the former. The addition of the former, *e.g.*, by the stings of insects, etc., is more likely to occur.

*The Effect of Dilution upon Carbonates.*

The calculation of the alkalinities of $Na_2CO_3$ may be made approximately by means of the hydrolysis constants (see p. 30, Chap. I.).

If $x$ is the fraction of the $Na_2CO_3$ which is hydrolysed, then

$$\frac{x^2C}{1-x} = K_h = \frac{K_W}{K_2}$$

$K_h = 1{\cdot}1 \times 10^{-4}$ (at 18°) $= 1{\cdot}9 \times 10^{-4}$ (at 25°).

The table is due to Auerbach (p. 296).

| $Na_2CO_3$ mols. | [OH′] millimols. | [OH′] per cent. of total C. | [OH′] millimols. | [OH′] per cent. of total C. |
|---|---|---|---|---|
| | At 18°. | | At 25°. | |
| 0·2 | 2·6 | 1·3 | 3·4 | 1·7 |
| 0·1 | 2·2 | 2·2 | 2·9 | 2·9 |
| 0·05 | 1·7 | 3·5 | 2·3 | 4·5 |
| 0·01 | 0·87 | 8·7 | 1·13 | 11·3 |
| 0·005 | 0·62 | 12·4 | 0·80 | 16·0 |
| 0·001 | 0·27 | 27·0 | 0·34 | 34·0 |

The hydrolysis of $NaHCO_3$ has been already discussed. The effect of dilution on [H·] begins to be apparent on the scale of the curve p. 287 at about $C = 0{\cdot}0001$. The [H·] of intermediate solutions is best obtained from equation (2*a*), p. 241, Chap. VI.

On introducing the values of K and $c$ these become at 18°

$$R = \frac{1 + \frac{12 \times 10^{-11}}{[H\cdot]} + \frac{0{\cdot}64 \times 10^{-14}\,(6 \times 10^{-11} + [H\cdot])}{[H\cdot]\,6 \times 10^{-11}\,C}}{1 + \frac{6 \times 10^{-11}}{[H\cdot]} + \frac{[H\cdot]}{3{\cdot}04 \times 10^{-7}}}$$

$$\text{or } R = \frac{2 + \frac{[H\cdot]}{6 \times 10^{-11}} + \frac{0{\cdot}64 \times 10^{-14}\,(6 \times 10^{-11} + [H\cdot])}{[H\cdot]\,6 \times 10^{-11}\,C}}{1 + \frac{[H\cdot]}{6 \times 10^{-11}} + \frac{[H\cdot]^2}{18{\cdot}24 \times 10^{-18}}}$$

From these equations the following values of [H·] have been calculated to supply the neutralisation curve of $H_2CO_3$ at C = 0·001 by the author (p. 239, Chap. VI.).

| | | | | | |
|---|---|---|---|---|---|
| R = | 0·0 | 0·03 | 0·23 | 0·60 | 0·75 |
| − log [H·] = | 4·75 | 5·00 | 6·00 | 6·70 | 7·00 |
| R = | 0·975 | 1·06 | 1·44 | 1·86 | 2·50 |
| − log [H·] = | 8·00 | 9·00 | 10·00 | 10·50 | 11·00 |

The effect of dilution does not make a difference of 0·1 in − log [H·] until the ratio R of alkali to acid is 1·3, *i.e.*, until 65 per cent. of the acid is neutralised. At 100 per cent. neutralisation the calculated − log [H·] is 10·63 (agreeing with that quoted from Auerbach above), and therefore a dilution from 0·1 to 0·001 has reduced − log [H·] by about 1·0 unit.

If the total concentration of $H_2CO_3$ is 0·0001 the effect of dilution is now 0·2 unit at 50 per cent. neutralisation ($NaHCO_3$) and about 1·6 units at 100 per cent. ($Na_2CO_3$). ($H_2CO_3$) = 0·0001.

| | | | | | |
|---|---|---|---|---|---|
| R = | 0·00 | 0·09 | 0·23 | 0·60 | 0·76 |
| − log [H·] = | 5·26 | 5·50 | 6·00 | 6·70 | 7·00 |
| R = | 0·98 | 1·12 | 2·01 | 3·62 | |
| − log [H·] = | 8·00 | 9·00 | 10·00 | 10·50 | |

*The Alkalinities of Hard Waters.*

(1) Saturated solutions of alkaline earth carbonates.—The total solubility of $CaCO_3$ (calcite) in air free water has been frequently determined with the following results :—

The dissolved $CaCO_3$ is highly hydrolysed (about 80 per cent.), giving $HCO'_3$ and OH′, and the total solubility is therefore greater than the square root of the solubility product, which is constant in the presence of solid calcite. It may be calculated from the equations expressing the

| Solubility in mgm. mols per litre. | Temperature. | Observer. |
|---|---|---|
| 0·13 | About 16° | Schloesing C.R. 74, 75 and 90 (1872 and 1880) |
| 0·13 | 18° | Kohlrausch and Rose |
| 0·10 | 8·7° | Ljiubavin |
| 0·125 | 23·8° | Ljiubavin |
| 0·113 | 100° | Fresenius |
| 0·166 | 16° | McCoy |
| 0·1433 | 25° | Kendall |
| 0·1504 | 50° | Kendall |
| 0·1779 | 100° | Kendall |

solubility of $CaCO_3$ in the presence of varying amounts of $CO_2$ (Bodlander, *Zeitsch. phys. Chem.*, 35, 25 (1900); McCoy, *J. Amer. Chem. Soc.*, 33, 468 (1911)).

The latter gives $Ca^{\cdot\cdot} \times CO''_3$ as $9{\cdot}3 \times 10^{-9}$, and this combined with his value of the total hydrolysed carbonate dissolved gives an exponent of nearly 10—agreeing with the value on the curve at $C = 0{\cdot}0001$ (which is practically the same as that at $C = 0{\cdot}00013$). The author has attempted to verify this alkalinity both by the electrometric and colorimetric methods, but the exponents found were somewhat low (9·4 to 10·0), probably on account of the extreme sensitivity of such solutions to traces of $CO_2$.

The carbonates $SrCO_3$ and $BaCO_3$ according to their solubilities should also give a decided pink with phenolphthalein. But in all these cases the actual alkalinity (roughly equal to that of about 0·0001 N. alkali) varies according to the nature of the solid phase, whether amorphous or crystalline, freshly precipitated or aged (see p. 321).

In the case of other slightly soluble carbonates (as that

of Mg), the existence of different hydrates, basic salts, or hydroxides often makes the calculation more involved.

(2) Dilute carbonate solutions in equilibrium with the air.

According to what has already been said (p. 309), dilute carbonate solutions, such as hard waters, which are in equilibrium with the air, must possess a perfectly definite alkalinity for a given concentration of total alkali. This alkalinity will be lower than that for the solutions of moderate to high concentration. In the case where solid carbonate is present the solubility will be increased by the atmospheric $CO_2$ until that concentration is reached which gives the equilibrium $[H_2CO_3]$. Solutions of all other concentrations will tend to lose $CO_2$ or to gain it from the air—the higher concentrations to lose $CO_2$ and deposit $CaCO_3$, the lower to gain it and dissolve $CaCO_3$.

The relation between $p$ of $CO_2$ (in atmospheres) and concentration of calcium carbonate, etc. (expressed as $y =$ grams $CaCO_3$ per litre), is given by the equation of Schloesing:

$$p^{0\cdot37866} = 0\cdot92128\,(y - 0\cdot0131).$$

This investigation was afterwards extended by McCoy, who used much higher pressures of $CO_2$. The calculated concentration of calcium carbonate in equilibrium with air ($p_{CO_2} = 0\cdot0003$ atmosphere) is 56 milligrams $CaCO_3 =$ 0·56 millimol per litre, or 5·6 degrees of hardness. If a water has a "temporary" hardness higher than this, the pressure of $CO_2$ must have been higher when the water was in contact with calcite. In contact with normal air such water would tend to lose $CO_2$ and deposits $CaCO_3$ on shells, rocks, sand and other solid nuclei. In the absence of these there is evidence that the supersaturation (with $CaCO_3$) after loss of $CO_2$ is easily maintained. Thus Walker and

Kay (below) found that a water of hardness 20 when treated with a current of normal air only showed a visible precipitation after several hours, and after 36 hours the hardness was still 9·6.

The effect of dilution upon the acidity of $CaCO_3$ solutions in equilibrium with the air has been studied by Walker and Kay, *J. Soc. Chem. Ind.*, 31, 1014 (1912). The solutions were all unsaturated with $CaCO_3$ at a mean temperature of about 15°. The colorimetric method was employed with phosphate solutions as standards and azolitmin as indicator. Any colour present in the water was compensated by making the light which illuminated the phosphate standard pass through a second Nessler tube containing the water (see p. 209, Chap. V.).

The results are expressed as relative acidities, *i.e.*, as multiples of $[H^{\cdot}] = (OH') = \sqrt{K_w}$ at the temperature. For the sake of comparison with other tables these relative acidities have been reconverted into the absolute values.

| Hardness as parts in 100,000. | Millimols $CaCO_3$ in 1 litre. | Relative acidity. | Relative alkalinity. | $[H^{\cdot}] \times 10^7$. |
|---|---|---|---|---|
| 0·25 | 0·025 | 2·3 | — | 1·7 |
| *0·5 | 0·05 | 1·5 | — | 1·1 |
| 1·0 | etc. | 1·0 | 1·0 | 0·74 |
| 2·0 | — | — | 2·3 | 0·32 |
| 4·0 | — | — | 5·8 | 0·13 |
| *5·0 | — | — | 7·5 | 0·099 |

The authors made certain that equilibrium was attained by proving that the final values of $[H^{\cdot}]$ after the aspiration of air were identical whether the original solution were acid or alkaline.

Some results were also given for $MgCO_3$.

| Hardness as parts $CaCO_3$ per 100,000. | Millimols per litre. | Relative acidity. | Relative alkalinity. | $[H\cdot]\times10^7$. |
|---|---|---|---|---|
| 1 | 0·1 | 1·0 | 1·0 | 0·74 |
| 2 | 0·2 | — | 1·9 | 0·39 |
| 4 | 0·4 | — | 4·2 | 0·18 |

Thus the $MgCO_3$ appears to give a slightly higher acidity than the $CaCO_3$ in equivalent concentration.

It is possible to obtain from these results the ratio of alkali to acid, and hence to test the result of the equations for dilute solutions, p. 241. For the degree of hardness gives both the total alkali and the carbonic acid, since it may be shown that the fraction of this which forms $H_2Co_3$ is negligible at the hydrion and total concentrations given. The $[H_2CO_3]$ should be that which is in equilibrium with the $CO_2$ of the air, *i.e.*, $1{\cdot}345 \times 10^{-5}$. It may also be calculated from the constant of the homogeneous equilibrium.

$$H_2CO_3 = \frac{[H\cdot][HCO_3']}{K_1}.$$

From the marked results* in the table above, the values of $H_2CO_3$ are $3{\cdot}3 \times 10^{-5}$ and $3{\cdot}6 \times 10^{-5}$. It has been noticed by several investigators that $H_2CO_3$ calculated from the homogeneous is slightly greater than that calculated from the heterogeneous equilibrium. Taking the former as more likely to be correct, the ratio R is 0·97 at $c = 0{\cdot}001$ and 0·73 at $c = 0{\cdot}0001$ (these being the two total $H_2CO_3$ concentrations of the marked values in the table). The calculated values of R from the equations, p. 241, or the curve at these concentrations are 0·98 and 0·75.

The general equations, then, for dilute solutions appear to be well supported by the few experimental results which

are available. Of the experimental magnitudes involved in the equations $[H^{\cdot}]$ is the most easily determined; from it R can be obtained and hence the total carbonic acid, since the total alkali is easily found by titration. From these, with the aid of the preceding equations $HCO'_3$, $H_2CO_3$ and all other concentrations may be calculated.

*The Titration of Carbonic Acid.*

There are three possible end points in the titration of mixtures of alkali and carbonate :—

(1) The whole of the carbonic acid is set free, and therefore the total alkali is determined. The end-point is acid and is found with an indicator of low exponent tropaolin 00 (Hiller, *Ber.*, 11, 460 (1878) ; methyl orange, Lunge, *Ber.*, 11, 1944 (1878); Kuster, *Zeitsch. anorg. Chem.*, 13, 127 (1897) ).

(2) The acid is added until all the alkali is present as bicarbonate. All the hydroxide and half the carbonate alkali is therefore determined. The bicarbonate end-point is obtained by the use of an indicator of moderately high exponent (Warder, *Amer. Chem. J.*, 3, 55 (1881); Lux, *Zeitsch. anal. Chem.*, 19, 457 (1880); Lunge and Lohofer, *Zeitsch. angew. Chem.* (1901).

(3) The addition of acid is stopped when all hydroxide is combined, and the hydroxide alkali is alone determined. Or by the reverse process alkali is added until the whole of the acid is converted into carbonate. In practice the carbonate end-point is obtained in the presence of a base forming a very slightly soluble carbonate (Winkler) (see p. 268, Chap. VI., and p. 322, this chapter).

(1) The possibility of the titration of the total alkali in carbonates depends upon the $[H^{\cdot}]$ produced by the $CO_2$ set free. If the titration is carried out in the cold, the highest possible $[H_2CO_3]$, corresponding to saturation with the gas,

will be about 0·05 molar. On account of the presence of the NaCl, the [H·] of this will be far greater than that calculated for $H_2CO_3$ of this concentration. Examples have already been given which show that the regular effect of the addition of neutral salts is to raise the acidity. This effect is particularly marked in the case of carbonic acid (Acree, *Amer. Chem. J.*, 36, 120 (1906)).

Even a few drops of a saturated solution of carbonic acid when added to a saturated sodium chloride solution containing methyl orange change the colour to orange, and a few more turn it pink (B. de Szyzskowski, *Zeitsch. phys. Chem.*, 58, 63, 73 (1907, 1908, 1910)). The colour of a solution saturated with both $CO_2$ and NaCl was the same as that of an acetic acid solution free from salt of 14 times the concentration. The constant of carbonic acid has therefore been increased to about 1,000 times its value in pure water. The correct titration value of [H·] varies with the salt concentration and may therefore be found most safely by the compensation method of Kuster (ref. p. 315). The comparison solution contains NaCl of the concentration which will be produced by the titration and is saturated with $CO_2$. The tint which is imparted to methyl orange which has been added in the same amount as to the titrate is the end-point colour. The necessity for this may, however, be obviated by the addition of sodium indigo sulphonate to the methyl orange. The colour then remains a pure yellow until all the carbonic acid is set free, when it becomes a green gray, which is almost colourless if the indicator is dilute, and is changed to violet on further addition of acid (Luther, p. 161, Chap. IV.; Kirschnick).

(2) It appears from the neutralisation curves that the bicarbonate point is suitable for titration; since the [H·] is almost independent of concentration, the exponent only changing from 8·4 to 8·2 when concentration changes from

0·1 to 0·0001. There are other causes, however, which have led to some uncertainty. In the first place the choice of phenolphthalein is not altogether a fortunate one, in view of the great effect of changes in the concentration of the indicator. The best concentration to employ is the higher one on p. 157, Chap. IV., *i.e.*, 20 drops of 0·05 per cent. to every 10 c.c. of solution when the titration is finished. Bjerrum (*Titrierungen*, p. 99) recommends practically the same concentration, *i.e.*, 0·3 c.c. of 1 per cent. to 100. As standard for comparison there may be used 3·7 HCl + 6·3 borate, exponent = 8·4. A solution of pure bicarbonate may be used as a standard, but it is more troublesome to prepare, not only because the solution tends to lose $CO_2$ (see p. 303), but chiefly because, as Thiel has shown, ordinary solid bicarbonate contains over 6 per cent. of $Na_2CO_3$. To improve the preparation it is recommended that the $NaHCO_3$ be treated with water saturated with $CO_2$, dried rapidly and washed with alcohol, then with ether saturated with $CO_2$. The preparation is analysed by heating about 3 grams in a current of air free from $CO_2$, and weighing the $H_2O$ and $CO_2$ in absorption tubes. The percentage of $NaHCO_3$ is calculated on the weight of $CO_2$ obtained. The percentage of $Na_2CO_3$ ought to be only about 0·6, and a solution of this preparation gives a pink which is pale but yet stronger than that of the comparison solution mentioned above. The pale pink is thus justified in another way, and it also lies at the indicator exponent of maximum sensitivity (see p. 173). The error in matching is about 0·2 in the exponent. Applying this to the curves, it is seen to correspond to about 0·02 in R at C = 0·1, and the amount of carbonic acid found is therefore correct to about 2 per cent.

If it is not desired to measure the indicator, so much may be added that no further colour is produced.

According to MacBain (p. 319) this first occurs at

saturation, *i.e.*, after the addition of about fifty to sixty drops of a 1 per cent. solution to 100 c.c. In this paper also comparison solutions are recommended, and especially the unalterable standards of colour made from copper and cobalt salts (see p. 208, Chap. V.). The accuracy is said to be about 0·1 per cent. and may rise to 0·01 per cent. with 40 c.c. of 0·2 N. solutions.

*The Titration of Dilute Solutions.*

If it is desired to titrate amounts of free $CO_2$ in mineral waters, etc., of the order 0·001 to 0·0001 molar, it is not admissible to use the relatively high concentrations of phenolphthalein recommended above. With a dilute phenolphthalein the first pink appears at a higher exponent, and the correct exponent is even a little lower on account of the dilution of the carbonate (see p. 287). An end-point somewhat on the alkaline side of $NaHCO_3$ may, of course, be chosen and standardised with the aid of one of the comparison solutions of Chap. V., the titre found being then always multiplied by a constant factor. Auerbach, *Zeitsch. angew. Chem.*, 25, 1722 (1912), recommends the use of $Na_2CO_3$ as the titrating liquid (Trillich method). Waters which contain about 1 millimol of free $CO_2$ and 0·5 of $NaHCO_3$ may be titrated by means of standard $Na_2CO_3$, after the addition of five drops of 0·002 per cent. phenolphthalein to 300 c.c. Another difficulty experienced in dilute solutions is due to the fact that this neutralisation is a "time reaction" (see p. 294, this chapter). In a dilute carbonate solution which has been rapidly titrated the pink colour (of phenolphthalein) first produced fades; after another addition of alkali it reappears and then fades again, and may thus require successive additions of alkali for as much as half an hour. In the case of other acids the colour first produced is permanent, or fades from the

top showing the effect of atmospheric $CO_2$, and not throughout the solution as in bicarbonate titrations.

The phenomenon has been investigated by MacBain, *J. Chem. Soc.*, 101, 814 (1912); Vorlander and Strube, *Ber.*, 46, 172 (1913); A. Thiel, *Ber.*, 46, 241, 867 (1913). It does not depend upon the phenolphthalein, for if sufficient time is given for the completion of the reaction the colour is permanent. It is probably due to the slow hydration of the dissolved $CO_2$ (p. 294, this chapter).

The time required is greater the greater the amount of base added (short of that required to form bicarbonate), being about 60 minutes with 2·29 millimols of $H_2CO_3$ and 2·09 of alkali at 15·5°. Small quantities of neutral salts have but a slight effect upon the velocity, but the reaction is retarded by the presence of $NH_4Cl$ and by fall of temperature. The remedy, when such conditions prevail, is to add a slight excess of alkali and titrate back.

*The Titration of Total Alkali in Dilute Carbonate Solutions.*

In the well-known titration of total carbonate in natural waters (Hehner method) the chloride produced is so dilute that it will not affect the "strength" of the carbonic acid liberated (see p. 316). The concentration of the acid is so low as to permit the use of an indicator of higher exponent than methyl orange, and the use of such is also desirable in order to reduce the considerable $H^{\cdot}$ error (see p. 254) caused by the high dilution.

Methyl red has been recommended by Kay and Newlands, *J. Soc. Chem. Ind.*, 35, 445 (1916). Since the end-point is slightly affected by the $CO_2$ even at the high dilution, the liberated acid must be removed.

The water (100 c.c.) is placed in a porcelain dish, titrated with N./50 HCl and methyl red (2 c.c. of a 0·005 solution of

the indicator in 80 per cent. alcohol*) until the colour changes, boiled for about a minute, and the titration continued until the red is permanent. Or the acid may be added in slight excess, the solution boiled for one minute and titrated back with N./50 baryta. The $CO_2$ may also be removed without heating by means of a current of air. The method has been tested on prepared waters containing either calcium or magnesium bicarbonates and gives results correct within 0·1 degree of hardness.

*Titration of the Second Hydrion of Carbonic Acid.*

(3) When a salt is present which is capable of forming by double decomposition an insoluble carbonate, the form of the second half of the neutralisation is changed, say from R = 1·8, the hydrogen exponent, R, gradient becoming very steep at the point R = 2·0. The effect then is to convert the second dissociation of $H_2CO_3$ into that of a strong acid. The nature of this action is definitely connected with the nature of the heterogeneous equilibrium. The observed high alkalinity of the normal salt is due to hydrolysis, and the addition of $BaCl_2$ reduces the absolute amount of alkali formed by reducing the total carbonate concentration down to the low value in equilibrium with solid $BaCO_3$. The alkalinity of such a solution according to equation (2*a*), p. 241, is perfectly definite if the solubility is known. It corresponds to a full pink with phenolphthalein according to Thiel (p. 321). This figure was obtained by titrating 500 c.c. of a 0·01 molar solution of $H_2CO_3$ in the presence of $BaCl_2$ of 0·02 molar concentration. An excess of $BaCl_2$ in the Winkler titration is required in accordance with the theory of Chap. VI., pp. 268 and 269. The excess by increasing ($Ba^{\cdot\cdot}$) diminishes ($CO_3''$) and therefore diminishes

* Made from absolute alcohol, free from acid.

the amount hydrolysed and also increases [H·]. This is desirable if it is required to use an excess of the indicator and to have an almost colourless solution at the end-point. A comparison solution chosen from Chap. V. or one saturated with $BaCO_3$ may also be used. According to the solubility products

$$[Ca^{\cdot\cdot}] \times [CO''_3] = 9{\cdot}3 \times 10^{-9}$$
$$[Sr^{\cdot\cdot}] \times [CO_3''] = 1{\cdot}57 \times 10^{-9}$$
$$[Ba^{\cdot\cdot}] \times [CO_3''] = 8{\cdot}1 \times 10^{-9}$$

(McCoy, *J. Amer. Chem. Soc.*, 33, 468 (1911)) the colour of the finished solution (and the comparison standard) will be about the same whether calcium or barium salts are used, but slightly less with strontium salts. An investigation by Thiel, however, into this point showed that the alkalinity is variable, on account of the different solubilities of the freshly precipitated and aged carbonates in each case. If $BaCO_3$ is freshly precipitated (*i.e.*, from $BaCl_2$ and $Na_2CO_3$) it gives a deeper pink with phenolphthalein than that which has been previously prepared (from solid $BaCO_3$) or has been precipitated and allowed to stand. Therefore the comparison solution should always have been prepared under the same circumstances and allowed to stand for the same time as that which is present in the solution to be titrated.*

The titration figure corresponding to the standard colour obtained will then be almost exactly twice that of the first bicarbonate titration carried out as described on pp. 316, 317.

This has been proved by the experiments of Thiel, *Sitzungsber. der Ges. z. Beford. d. Gesamten Naturwiss. Marburg* (1912), 118.

* The paling of the pink of phenolphthalein due to ageing of $BaCO_3$ begins to be perceptible in about an hour.

About 50 c.c. of saturated $CO_2$ solution were pipetted into about 150 c.c. of water, to which about 9/10 of the alkali required for bicarbonate had been added previously and also 1 c.c. of 1 per cent. alcoholic phenolphthalein. Then 0·4826 N. NaOH was added (I.) to the first perceptible pink; (II.) to the same pink as that of a solution of $NaHCO_3$, purified as on p. 317; (III.) after the addition of 5 c.c. of 0·5 molar $BaCl_2$, to the same colour as that of a standard solution prepared by precipitation of $Na_2CO_3$ with excess of $BaCl_2$.

*C.c. NaOH required.*

| I. | II. | III. |
|---|---|---|
| 3·94 | 4·03 | 8·01 |
| 3·88 | 3·96 | 7·85 |
| 3·92 | 4·00 | 7·89 |

The Winkler titration may also be carried out in the presence of $CaCO_3$ — $CaCl_2$ being added to the bicarbonate and then titrated with alkali, or the $CO_2$ solution may be added to excess of $Ca(OH)_2$ and the free alkali titrated with acid. It was found that freshly precipitated $CaCO_3$ gives a more intense colour with phenolphthalein than $BaCO_3$ does. Also the process of ageing is rather slower. Care must be taken that the solution is not supersaturated, which will give a still more intense red with phenolphthalein. If the $Na_2CO_3$ is only 0·002 molar, the $CaCl_2$ 0·007 molar, no precipitate is obtained, although the amount of $CaCO_3$ in solution is about fifteen times the solubility when in contact with $CaCO_3$. The best of the carbonates for the above purpose is probably $SrCO_3$. It has the smallest solubility, and the ageing is rapid, the phenolphthalein changing from deep red to almost colourless in a few minutes.

*Application of the Theory of Titration Errors to Titrations of Carbonates and in the presence of Carbonates.*

*The Bicarbonate Titration.* — The best value of the exponent at the bicarbonate end-point will be

$$\frac{\log K_1 + \log K_2}{2} = 8{\cdot}4.$$

The $H_2CO_3$ and $CO''_3$ errors are at this point equal to one another.

$$\frac{T[H^{\cdot}]}{K_1} = \frac{TK_2}{[H^{\cdot}]} = T.10^{-1{\cdot}85} = \frac{T}{70} \text{ c.c.}$$

Thus the probable error is more than 1 per cent. of the total alkali required.

*The Titration of Total Alkali in presence of Carbonates.*— The problem is, to exclude the carbonic acid from the titration and at the same time not to introduce too large a hydrion error. If the finished solution remains saturated with $CO_2$ at atmospheric pressure, then 50 c.c. of the solution is equivalent to 12·5 c.c. of 0·2 N. acid. If the $HCO'_3$ error is to be below 0·03 c.c., then

$$T\frac{K_1}{[H^{\cdot}]} = 12{\cdot}5\frac{10^{-6{\cdot}52}}{[H^{\cdot}]} < 0{\cdot}03$$

$$\text{and } [H^{\cdot}] = 10^{-3{\cdot}9}.$$

If the $[H^{\cdot}]$ error is also to be below 0·03 c.c.

$$0{\cdot}03 > \frac{V}{0{\cdot}2} \cdot 10^{-3{\cdot}9} \quad V < 50 \text{ c.c.}$$

As before it is seen that methyl orange is suitable—also the volume should be not more than 50 c.c. The percentage

accuracy depends, of course, upon the total amount of alkali in the carbonate or of strong acid which is to be titrated in presence of carbonic.

In practice this calculation gives too favourable a result if much neutral salt is present in the titrated solution, for, according to p. 324, the actual value of $K_1$ is much greater than $10^{-6\cdot52}$.

The possibility of titration of weak acids containing small quantities of $CO_2$, or with alkali containing carbonate, can also be estimated.

The equilibrium between atmospheric $CO_2$ and water has been already discussed (p. 296). The theoretical concentration of $H_2CO_3$ (about $1\cdot3 \times 10^{-5}$ mols at 15°) appears to be often exceeded in practice (see section on water free from $CO_2$). Treadwell ("Analytical Chemistry") estimates it as equivalent to 0·5 to 1·8 c.c. of N/10 KOH in every 100 c.c. of water ($5 \times 10^{-4}$ to $18 \times 10^{-4}$ mols $H_2CO_3$), McBain (p. 319) as equivalent to 0·03 c.c. of N/10 KOH ($3 \times 10^{-5}$ mols $H_2CO_3$). These quantities must either be eliminated from the water used, or conditions must be chosen so that they have no effect. The weaker the acid which is being titrated the more the result is vitiated by the presence of $CO_2$. By means of the formula

$$c_{H_2CO_3} = T \frac{K_1}{[H\cdot] + K_1} = 0\cdot03$$

the amounts of $H_2CO_3$ (as c.c. of the titrant) may be calculated which can be present if the error due to it is not to exceed 0·03 c.c. The first column gives the hydrogen exponent; the second the amount of $H_2CO_3$ (as c.c. of the titrant) which may be present if the error is not to exceed 0·03 c.c.; the third the error (*i.e.*, carbonic acid included in the titration) expressed as a fraction of the total carbonic acid present.

| Hydrogen exponent. | Amount of $CO_2$. | Fraction of $CO_2$ included in the titration. |
|---|---|---|
| 4 | 10 c.c. | 0·003 |
| 5 | 1 | 0·03 |
| 6 | 0·1 | 0·3 |
| 7 | 0·03 | 1 |
| 8 | 0·03 | 1 |
| 9 | 0·03 | 1 |
| 10 | 0·02 | 1·5* |

The appropriate indicators for column 1 may be obtained from Table III, Chap. IV.

The presence of even 2 or 3 per cent. of carbonate in alkalies makes an error of only about 0·2 per cent. when methyl red is used. Litmus (to red) shows about one-third of the carbonic acid present. The greatest possible amounts of carbonic acid which are permissible in titrating acids of various constants follow at once from the discussion and diagrams of Chap. VI.

* Some $R_2CO_3$ present at end-point.

# CHAPTER VIII

## A SUMMARY OF THE PRINCIPAL PROPERTIES OF SOME INDICATORS ARRANGED IN THE FOLLOWING GROUPS

Diazo and nitro compounds (methyl orange, nitrophenol)—Phthalein compounds (phenolphthalein)—Amino phenol methane (methyl violet)—Anthraquinone (alizarin)—Other indicators, including those of uncertain composition and natural origin.

In these classified lists a brief summary has been given of the hydrogen exponents and other properties of which a fuller account may be obtained from the preceding chapters by reference to the index. The absorption spectra are given in some cases. Other indicators not previously mentioned have also been included, and some special details have been given as to methods of preparation, strength of stock solutions, and other conditions of use.

### *Test-papers.*

It is sometimes more convenient or necessary to apply the indicators in the form of test-papers, *e.g.*, in the following cases:—

(*a*) When gases are to be tested for traces of acid or alkali;

(*b*) When some of the compounds in solution, *e.g.*, $H_2S$ liberated during a titration, would decolourise the indicator or otherwise falsify the results;

(*c*) When on account of the strong colour or turbidity of the solution the colour changes cannot be seen distinctly.

The best indicators to use for purpose (*a*) would appear to be those which are changed by the smallest amounts of

acid or alkali dissolving in the moisture of the paper. And as a matter of fact most of the test-papers which are most largely used are prepared from indicators with exponents in the neighbourhood of 7. Since the positive evidence of a definite colour change is required, papers must be prepared of both the acid and the alkaline colour. Of course, if these are highly sensitive they must be carefully preserved from contact with ordinary air in well-stoppered bottles. The preservation of the acid or alkaline colour of indicators with low or high values of $p_I$ would be difficult in theory, since they must require a high [H·] or [OH′] in the dry paper. And in practice it is found that, *e.g.*, blue congo paper which requires a low hydrogen exponent must be previously soaked in dilute sulphuric acid, then dried, dipped in the acid indicator solution, and dried again if it is to retain its colour. Even so it is very sensitive to alkalies, being changed even by the carbonates present in ordinary water.

In cases (*b*) and (*c*), where the papers are dipped into the solution or otherwise wetted with it, it appears probable that the changes occur at the exponents already given. Also it is seen by comparing the tables of sensitivity of papers with those of indicators in solution that they occur at the same concentrations of strong acids and bases when the former, as when the latter, method is used, *i.e.*, from 0·0005 to 0·0001 normal. For reasons already given the comparison can only be rough ; all that is proved is that the sensitivity of the papers is sufficient for most purposes.

*Preparation.*—Thin filter paper of rather tough quality or good note paper (which has been previously washed in distilled water and dried) is immersed in the neutral acid (sulphuric) or alkaline solution of the indicator. It is hung up to dry in a neutral atmosphere, and reversed at intervals

in order to distribute the colour. The colour changes will, as already stated, occur at the same exponents as when the indicator is in solution provided the paper is not very porous. But when a drop of a solution, *e.g.*, of a hydrolysed salt, is placed upon a bibulous test-paper, the acid or alkaline effect at the edges of the spot tends to be enhanced on account of the fact that the diffusion of the $H^{\cdot}$ or $OH'$ is more rapid than that of the other ions present.

A few of the more important test-papers have been mentioned after the accounts of the indicators from which they are made.

*Methyl Orange* $(CH_3)_2=N-C_6H_4-N_2-C_6H_4-SO_3Na$. The sodium salt of dimethylamino azo-benzene sulphonic acid. The free acid is generally called helianthin. The names orange III, mandarin orange, tropaolin O, dimethyl-aniline orange, have also been used.

$p_I = 4$ Range $= 2{\cdot}9$ to $4{\cdot}0$ (Sorensen)
$2{\cdot}7$ to $5{\cdot}4$ (Fels)

| Exponent | $<3$ | 4 | 5 |
|---|---|---|---|
| Colour | red | orange | yellow |

*Preparation.*—By the action of dimethylaniline upon diazo-benzene sulphonic acid in HCl solution. The sulphonic acid is made by dissolving sulphanilic acid, $C_6H_4(NH_2)SO_3H$, in sodium carbonate and diazotising with $NaNO_2$.

Or dimethylamino azo-benzene is prepared by adding about equimolecular weights of aniline and dimethylaniline to a weight of concentrated HCl equal to the sum of the two, dissolved in about fifteen times its weight of water. Sodium nitrite (about $\frac{1}{3}$ of the weight of the HCl) and NaOH (about $\frac{1}{6}$ of the weight of the HCl) are dissolved in about five times their weight of water and added gradually. The precipitate is redissolved in HCl, reprecipitated with NaOH, washed and crystallised from hot alcohol. The

DIAGRAM I.

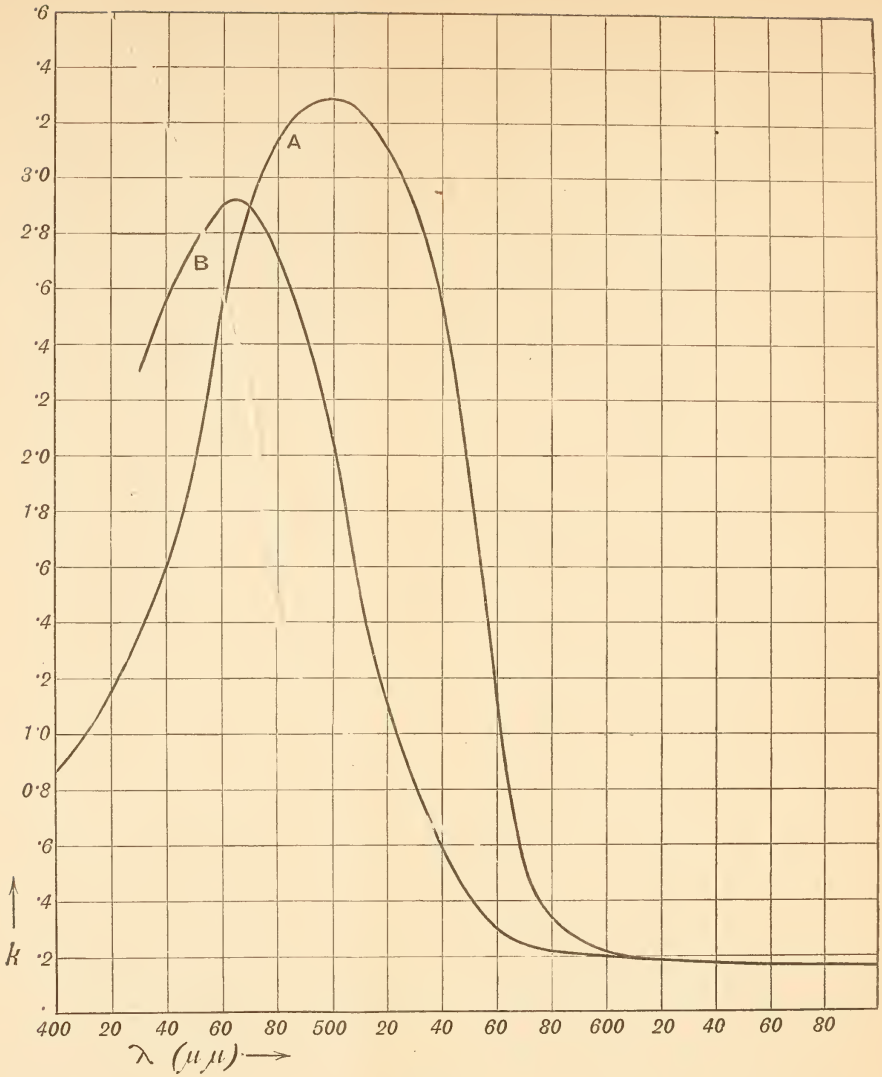



TABLE I.

(1) *Methyl Orange.*

A 0·005 per cent. in 0·002 N. HCl.
B 0·005 per cent. in 0·002 N. NaOH.

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| λ = 410 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 500 | 10 | 20 | 30 | 40 | |
| *k* (A) = 0·98 | 1·13 | 1·35 | 1·68 | 1·96 | 2·45 | 2·90 | 3·12 | 3·25 | 3·28 | 3·25 | 3·08 | 2·91 | 2·53 | |
| *k* (B) = | | 2·30 | 2·55 | 2·75 | 2·90 | 2·90 | 2·70 | 2·40 | 2·02 | 1·51 | 1·10 | | 0·60 | |
| λ = 50 | 60 | 70 | 80 | 90 | 600 | | | | | | | | | |
| *k* (A) = 1·90 | 1·10 | 0·55 | 0·33 | | 0·21 | | | | | | | | | |
| *k* (B) = | 2·28 | | | | 0·20 | | | | | | | | | |

dimethylamino azo-benzene is sulphonated by dissolving it in excess of concentrated sulphuric acid, pouring the solution into water, and converting the compound into the sodium salt.

This preparation, or the commercial product, may be purified by recrystallising from hot water. Some samples require to be purified by the addition of hydrochloric acid to a hot, strong solution. The precipitate is washed and dissolved in ammonia.

The stock solution may have various concentrations. The following have been recommended: 0·05 gram in 100 c.c. of water (Glaser); 0·1 gram to 1 litre, of which 3 to 5 drops are used for 10 c.c. solution (Sorensen); 0·1 per cent. in water, of which 0·1 c.c. is added to 100 of solution (Bjerrum). The concentration of the indicator in the solution must not be above that at which the solution in acids has a distinct orange tint. The colour is strong, and the change is better marked in a very dilute solution. Methyl orange is the typical and favourite indicator of acid change-point. Although it may occasionally (*e.g.*, when the salt of a strong acid and weak base is to be present at the end-point) give stoichiometrically accurate results, still this is not usually the case, and a correction must be applied to the results of titrations of strong acids with strong bases (see pp. 245, 246). The wide range of the change interval and the low value of the hydrogen exponent cause the change to be indefinite when the concentrations of strong acid and alkali are below about 0·01 N. The limits of concentration permissible are given by the theory of the hydrion error, p. 252.

It is also suited for the titration of weak bases with strong acids (p. 248) * and of strong acids in the presence

* The $p_{\mathrm{H}}$ value of methyl red is closer to the correct titration exponent of Kjeldahl distillate than is that of methyl orange. See Chap. VI., p. 232.

of weak acids (see p. 247). The neutralisation of an acid with an alkali is said to give a sharper end-point than the reverse process. In most cases the results could be much improved by the use of comparison solutions.

The colour of methyl orange is affected by $SO_2$ when this is set free by acids, but not by $SO_2$ already present in solution nor by $H_2S$ under the same conditions.

Alkalies containing sulphites may be boiled with $H_2O_2$ previously neutralised with alkali and then titrated as usual.

The indicator is decolourised by nitrous acid. The titration of nitric in the presence of nitrous acid may, however, be carried out if fresh methyl orange is added to the solution when nearly neutral.

It may be stated generally that methyl orange can be used in the titration of all acids which, in concentration below the required limit of error, and in presence of their own salts in the concentration produced by the titration, have a (negative) hydrogen exponent less than or equal to $p_I$. Also it may be used in the titration of the total alkali in salts of acids that, in the concentration in which they are set free during the titration, have an exponent greater than $p_I$.

These generalisations apply of course in their degree to all indicators of $p_I$ less than 7. They are in all cases subject to the reservation that the acids or bases in question have no specific influence on the indicator such as those mentioned above.

*Ethyl Orange*, $(C_2H_5)_2 = N - C_6H_4 - N_2 - C_6H_4 - SO_3Na$, or diethylaniline orange, is prepared from diethylaniline by a method similar to that used for methyl orange, which it resembles in most respects. The colour change is not quite so well marked. A solution containing 0·05 to 0·2 per cent. of the indicator in water or aqueous alcohol is suitable.

*Dimethylaminoazo-benzene*, $(CH_3)_2=N-C_6H_4-N_2-C_6H_5$, or butter yellow.

$$\frac{K_W}{K_B}=1\times10^{-3} \quad K_B=1\times10^{-11}$$

$p_I = 4{\cdot}2$ (Noyes). Range = 2·9 to 4·0 (Sorensen)

—— 2·5 ———— 3·5 ——

crimson flesh-coloured yellow.

*Preparation.*—See Methyl Orange.

Diazo-benzene chloride is prepared by dissolving 9·3 grams of aniline in 30 grams of 25 per cent. HCl. To the cooled and diluted solution is added a solution of 7 grams of $NaNO_2$.

The mixture is poured into a solution of 12 grams of dimethylaniline in 15 grams of the same HCl. Sodium acetate is added until there is no free HCl present. The product when recrystallised from alcohol appears as yellow crystals melting at 115°.

A solution containing about 0·05 per cent. of the indicator in alcohol may be used. Or 0·1 gram of the indicator is dissolved in 1 c.c. of 0·1 N. HCl + 1·99 c.c. of water + 800 c.c. of alcohol, and 5 to 10 drops of this are added to 10 c.c. of the solution (Sorensen). The transition of colour is somewhat sharper than that of methyl orange.

*Methyl Red*, $(C\overset{4}{H}_3)_2=N-C_6H_4-N_2-C_6H_4-COOH$, Dimethylamino azo-benzene ortho carboxylic acid.

$K_A = 1{\cdot}05\times10^{-5}$ $K_B = 3\times10^{-13}$ (Tizard).

$p_I = 5{\cdot}5$ (Bjerrum), 6 (Noyes).

Range 4·2 to 6·3 (Sorensen).

5·7 7·0

Red transition yellow.

Recommended by Rupp and Loose, *Ber.* 41, 3905 (1908).

*Preparation.*—T. F. Winmill's method has been described by Tizard (p. 145).

Anthranilic acid (5 grams) is dissolved in a mixture of 150 c.c. of water and 15 c.c. of concentrated HCl. To this 2·5 grams of $NaNO_2$ are added.

The solution is kept for half an hour and then poured into a mixture of 5 c.c. of concentrated hydrochloric acid, 50 c.c. of water, and 4·65 grams of dimethylaniline. Sodium acetate (50 grams) is added, and on warming to 40° the red product quickly separates, although the reaction does not appear to be complete for about three hours. The substance is then collected and can be recrystallised from glacial acetic acid. The yield is almost quantitative.

*Stock Solution.*—The concentration may be 0·02 to 0·1 per cent. in water. From 2 to 4 drops of the former are added to 100 c.c. of solution.

The hydrogen exponent of this indicator coincides with that which is according to the theory of Bjerrum the optimum on the acid side of neutrality (see p. 253).

It could with much advantage replace methyl orange for many purposes.

*Tropaolin O*, p. benzene azo resorcin sulphonic acid, $HSO_3 - C_6H_4 - N_2 - C_6H_3(OH)_2$.

$p_1 = 11{\cdot}5$. Range 11·1 to 12·7.

$-0{\cdot}3 \longrightarrow 4 \longrightarrow 12 \longrightarrow 15$

yellow green-yellow red-orange.

*Preparation.*—By the action of p. diazo-benzene sulphonic acid on resorcin or by the sulphonation of dihydroxy azobenzene. The solution may contain 0·1 gram to 1 litre, and of this 5 to 10 drops are added to 10 c.c.

*Properties.*—The compound is, as seen from its constitution, a strong acid. It crystallises in black needles which are reddish by transmitted light. The salts are orange.

DIAGRAM - II.

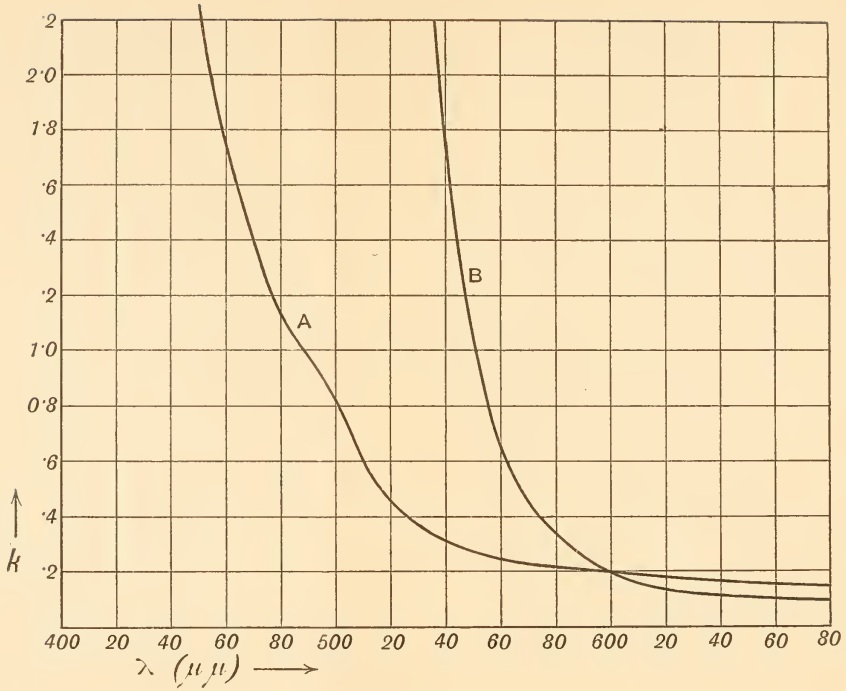



TABLE II.

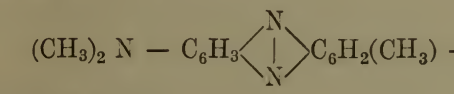
(2) *Tropaolin O.*

A 0·01 per cent. neutral.
B 0·01 per cent. 0·1 N. NaOH.

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| λ = | 450 | 60 | 70 | 80 | 90 | 500 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 600 |
| *k* (A) = | 2·28 | 1·78 | 1·40 | 1·13 | 0·99 | 0·82 | | 0·45 | | | | | | | | 0·20 |
| *k* (B) = | | | | | | | | | 2·85 | 1·65 | 1·00 | 0·65 | | 0·33 | | 0·20 |

By virtue of its second change this indicator can be used for the approximate titration of very weak acids or for finding the exponent in alkaline solutions by the match method.

*Neutral Red*, or toluylene red,



Range 6·8 to 8·0.

| | | |
|---|---|---|
| — 0·3 ⟶ 0 — | | 8 — |
| blue ⟶ blue-violet red | | orange ⟶ yellow |

occurs as orange red needle-shaped crystals or as a dark powder.

The commercial product (0·1 gram) is dissolved in 500 c.c. of alcohol and 500 c.c. of water and 10 to 20 drops are added to 10 c.c. (Sorensen). A typical neutral point indicator with a sharper colour change than rosolic acid.

*Tropaolin OOO*, or orange II, $\beta$ naphthol yellow, $HO_3S - C_6H_4 - N_2 - C_{10}H_6OH$, $\beta$ naphthol azo-benzene sulphonic acid or para-benzene sulphonic acid azo $\beta$ naphthol.

Range 7·6 to 8·9.

Change points given under tropaolin in Salm's table.

| | | | | | |
|---|---|---|---|---|---|
| — 0·3 | 0·0 ⟶ | 7 → | 8 ⟶ | 9 ⟶ | 14 |
| pink | yellow | flesh-coloured | pink | | violet. |

*Preparation.*—By the action of $\beta$ naphthol on p. diazo-benzene sulphonic acid.

Or the sodium salt of sulphanilic acid is prepared by dissolving (say $\frac{1}{10}$ mol) in the theoretical amount of $Na_2CO_3$ or NaOH (about 1 per cent. solution).

The cooled mixture is acidified with concentrated HCl, and normal $NaNO_2$ solution is run in until free $HNO_2$ can

no longer be detected with KI and starch paper. An alkaline solution of naphthol containing $\frac{1}{10}$ mol of this compound and of sodium hydroxide is prepared, and the other solution is added to this. The compound is salted out with sodium chloride.

The indicator orange II, *a* naphthol orange, may be prepared in the same way from *a* naphthol.

The acid forms black leaves with a greenish lustre. The sodium salt is red-brown. A saturated solution may be used or a 0·01 N. solution of which 4 to 10 drops are added to 10 c.c.

The alkaline pink is a stronger colour than the acid yellow.

*Tropaolin OO*, $\overset{1}{HO_3S} - C_6H_4 - \overset{4}{N}\overset{1}{=}N - C_6H_4 - \overset{4}{N}HC_6H_5$. Also called orange IV, diphenylamine orange, is phenylamino azo-benzene sulphonic acid (p. benzene sulphonic acid azo-diphenylamine).

$p_I = 2{\cdot}5$. Range = 1·4 to 2·6 (Sorensen).

| − 0·3 | 1 | 2 | 3 |
|---|---|---|---|
| red-violet | pink | flesh-colour | yellow. |

*Preparation.*—By treating an acid alcoholic solution of diphenylamine with p. diazo-benzene sulphonic acid.

Or phenylamino azo-benzene is heated for several hours at about 70° with an excess of fuming sulphuric acid.

The mixture after being cooled is poured into about 10 times its bulk of water. The precipitate is converted into the sodium salt and recrystallised three times from water. The free acid comes down as a violet-black precipitate when excess of HCl is added to the solution of its salts.

The stock solution may be 0·01 per cent., of which 3 to 5 drops are added to 10 c.c. Or 0·05 gram is dissolved in 100 c.c. of 50 per cent. alcohol and about half a c.c. added to 50 of solution.

It is a typical acid insensitive indicator which may be used for detecting strong acids in the presence of weak (see p. 221); or instead of methyl orange in the titration of total acids in carbonates (Hiller, *Ber.* 11, 460 (1878) ). The hydrion error will, however, be rather high.

*Metanil Yellow*, $HO_3S^{1} - C_6H_4^{3} - N_2^{1} - C_6H_4 - NHC_6H_5^{4}$, is the corresponding meta-sulphonic acid. Range 1·2 to 2·3.

The preparation is effected by a similar method, and the properties are similar.

*Alizarin Yellow G, or GGM*, $O_2N - C_6H_4 - N_2 - C_6H_3(OH) - COOH$, para-nitro-benzene azo-salicylic acid (sodium salt). Range 10·1 to 12·1. (See over page.)

*Preparation.*—Para-nitro-diazobenzene is combined with salicylic acid. This compound gives redder shades than that prepared from diazotised metanitraniline.

The commercial compound (0·1 gram) is dissolved in 1 litre of water, and 5 to 10 drops are added to 10 c.c.

*Monosulphonic Acid of para-nitro-benzene azo a naphthol*,

$$\begin{matrix} HO_3S^{3} \\ O_2N^{4} \end{matrix}\!\!\rangle C_6H_3 - N_2 - C_{10}H_6OH.$$

Recommended by Hewitt, *Analyst*, 33, 85 (1908).

The indicator is yellow in acid, purple in alkaline solution.

6 *Sulpho a naphthol* 1 *azo meta hydroxy-benzoic acid.*

Mellet's indicator, Lausanne.

The change points have been determined by Walpole (p. 206).

| 7 | 8 | 12 | 13 |
|---|---|---|---|
| orange | blue | violet | red. |

DIAGRAM III.

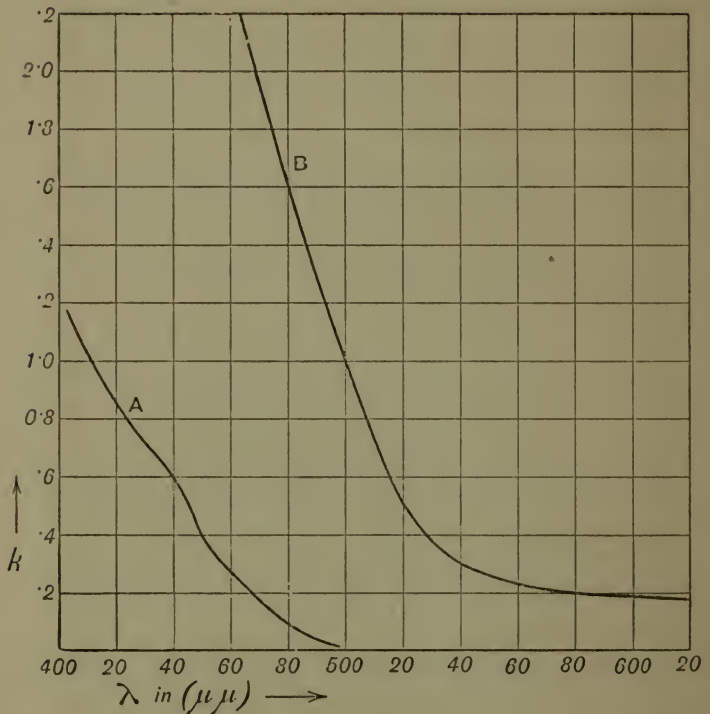



TABLE III.

(3) *Alizarin Yellow.*

A 0·01 per cent. neutral.
B 0·01 per cent. 0·001 N. NaOH.

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| λ = 410 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 500 |
| *k* (A) = 1·05 | 0·85 | 0·72 | 0·60 | 0·38 | 0·28 | 0·19 | 0·09 | 0·03 | |
| *k* (B) = | | | | | | 1·96 | 1·63 | 1·30 | 1·02 |
| λ = 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 600 |
| *k* (B) = 0·73 | 0·52 | | 0·30 | | | | | | 0·20 |

The sodium salt is very soluble in water, and the colours are intense.

DIAGRAM IV.

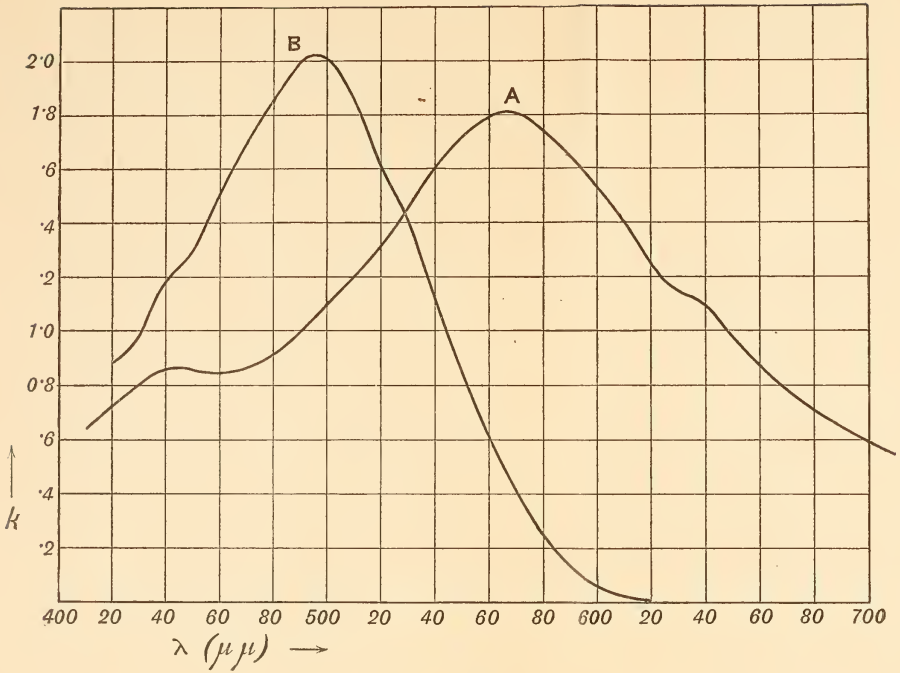


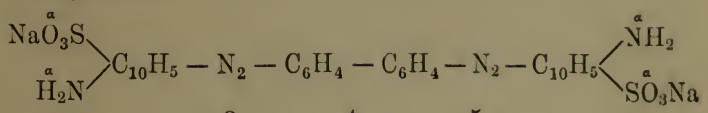

TABLE IV.

(4) *Congo.*

A 1/20,000 0·001 N. HCl.
B 1/20,000 0·001 N. NaOH.

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| λ = 410 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 500 | 10 | 20 | 30 | 40 | 50 | |
| *k* (A) = 0·65 | 0·73 | 0·78 | 0·87 | 0·86 | 0·83 | 0·86 | 0·90 | 1·00 | 1·08 | 1·20 | 1·32 | 1·46 | 1·61 | 1·71 | |
| *k* (B) = | 0·88 | 0·99 | 1·19 | 1·29 | 1·52 | 1·70 | 1·85 | 2·00 | 2·01 | 1·85 | 1·60 | 1·42 | 1·10 | 0·79 | |
| λ = 60 | 70 | 80 | 90 | 600 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 680 | 710 | | |
| *k* (A) = 1·78 | 1·80 | 1·73 | 1·64 | 1·53 | 1·40 | 1·24 | 1·15 | 1·09 | 0·98 | | | 0·71 | 0·55 | | |
| *k* (B) = 0·60 | 0·40 | 0·13 | 0·23 | 0·05 | | | | | | | | | | | |

*Congo Red.*



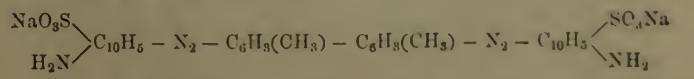
3 4 5

blue violet scarlet.

*Preparation.*—Benzidine, $NH_2-C_6H_4-C_6H_4-NH_2$, is converted into tetrazo-benzidine chloride, and this is combined in acid solution with 2 mols of sodium naphthionate in two stages. The combination of the second molecule is not complete for several days. The sodium salt is a red-brown powder soluble in water, only slightly soluble in alcohol. The blue acid is precipitated from moderately concentrated solutions by mineral acids, and the red salt by excess of sodium hydroxide, but the salt is redissolved by water.

The sodium salt (0·5 gram) is dissolved in 90 c.c. of water + 10 c.c. of alcohol. Or a 1 per cent. solution is made in 30 per cent. alcohol, and 1 drop is added to 10 c.c. The alcohol is added in order to prevent the precipitation of the blue acid by acids. The change from blue to red is easier to observe than that from red to blue. According to its change-point it is insensitive to acids, but is much used for titrating aniline bases and alkaloids. It is much affected by neutral salts, especially by those of the calcium group, and also by proteins. One reason of its popularity is probably the conspicuousness of the change of colour.

*Benzopurpurin B.*



— 0·3 1 to 2 3 4 5 14

blue violet red-violet red red-yellow ⟶ pink.

1. 2

*Preparation.*—By the action of nitrous acid upon tolidine, $H_2N - C_6H_3(CH_3) - C_6H_3(CH_3) - NH_2$, tetrazo ditolyl chloride is produced, and this is combined with two molecules of $\beta$ naphthylamine $\beta$ sulphonic acid.

It may be purified by precipitating the commercial sodium salt with HCl, drying at 100° and shaking a little of the solid with dilute alkali insufficient to dissolve it. It is similar to congo red but has a larger range and a lower exponent of half-way change.

*Paranitrophenol*, $C_6H_4\begin{matrix}NO_2\\OH\end{matrix}$

$p_1 = 6{\cdot}0$.

Range 4·0 to 6·5 (Noyes).

,, 5·0 to 7·0 (Sorensen).

| 5 | 6 | 7 |
|---|---|---|
| colourless | greenish | green-yellow. |

*Preparation.*—Phenol (1 part) is run into a mixture of 2 parts of nitric acid and 4 parts of water. Or a warm solution of phenol with a little alcohol is run into a mixture of sodium nitrate and sulphuric acid. The dark-coloured oil is freed from excess acid by rinsing with water, more water is added, and the ortho compound is distilled in a current of steam with a warm condenser (this compound melts at 45°). The residue is extracted with hot dilute hydrochloric acid, evaporated to small bulk and acidified more strongly. The crystals which form on cooling melt at 114°. They may be purified and recrystallised from hot water.

A 0·2 per cent. alcoholic solution may be used. On account of its pale colour it is not suitable for the titration of brownish solutions.

It is scarcely affected by proteins and has no tendency to pass into a colloidal state.

DIAGRAM V.

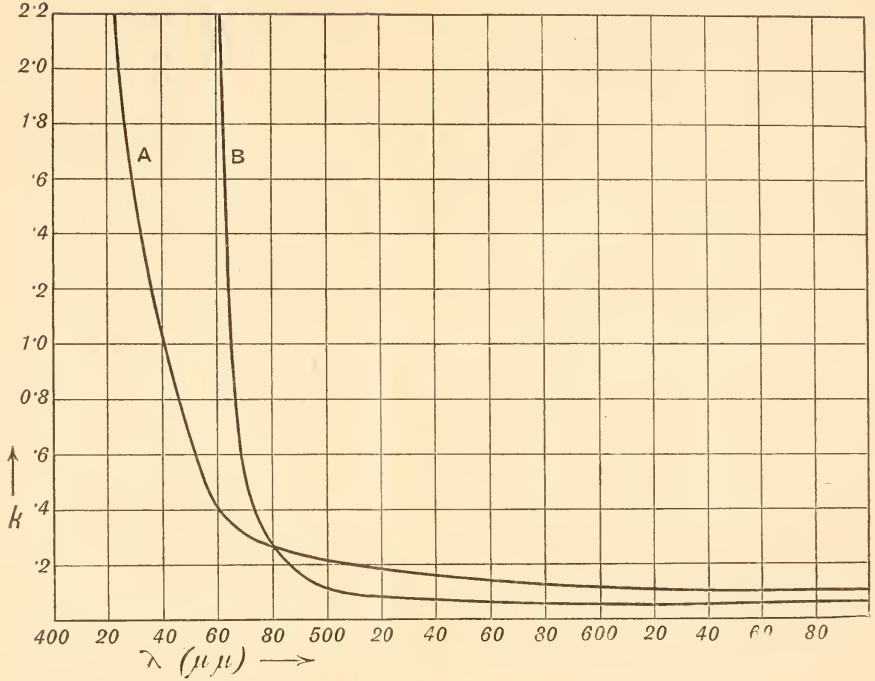



TABLE V.

(5) *p. Nitrophenol.*

A 1·0 per cent. neutral.
B 0·01 per cent. 0·01 N. NaOH.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $\lambda$ = | 430 | 40 | 50 | 60 | 70 | 80 | 90 |
| $k$ (A) = | 1·52 | 1·00 | 0·68 | 0·40 | 0·32 | | 0·25 |
| $k$ (B) = | | | 2·79 | 2·22 | 0·53 | 0·26 | 0·15 |

*Trinitrobenzene*, symmetrical 1, 3, 5.

$C_6H_3(NO_2)_3$

| | | | |
|---|---|---|---|
| —0·3 to 12 | 13 | 14 | 14·3 |
| colourless | orange | reddish | nearly colourless. |

*Preparation.*—Metadinitrobenzene is nitrated for three days at 100°—120° with a mixture of 3 times its weight of concentrated nitric acid and $7\frac{1}{2}$ times its weight of fuming sulphuric acid.

The product is precipitated by the addition of water, washed free of acid with dilute alkali and recrystallised from alcohol. The pure substance melts at 122°. A 0·1 to 0·5 per cent. solution in alcohol may be made up and rather more than usual of this solution is taken, as the red with alkalies is not a strong colour.

2, 6 *dinitro* 4 *aminophenol*, or isopicramic acid (Meldola and Hale, *Chemical World*, 1, 327 (1912) ).

| | | |
|---|---|---|
| 4·1 | —— | 5·6 |
| pink | orange | yellow. |

According to its exponent, the indicator might be used as a substitute for methyl red.

*Phenolphthalein.*

$p_1 = 9.$

Range 8·4 to 9·2 (Noyes) } according to the
8·3 to 10·0 (Sorensen) } concentration.

*Preparation.*—Phthallic anhydride is heated for several hours at about 120° with twice its weight of phenol and $\frac{1}{3}$ of its weight of concentrated $H_2SO_4$, and the yellow residue is washed with water, dissolved in dilute alkali and filtered. The compound may be reprecipitated with a little acid, washed, dried and used in this condition. Or it may be further purified by boiling an alcoholic solution with animal

charcoal, adding water (but not enough to precipitate the compound), filtering off any resinous substance and evaporating on the water bath. It appears as white crystals melting at 250°.

The stock solution may be from 0·1 per cent. to 1 per cent. in alcohol or aqueous alcohol (down to 50 per cent.). If the solution is dilute it is desirable to correct the acidity of the alcohol by adding very dilute alkali (0·01 N.) to palest pink and then acid (0·01 N.) to colourless.

The colour change is easily seen both by daylight and artificial light, and is rather better in the direction colourless to pink than *vice versâ*. The effects of alcohol, neutral salts, etc., have been already given.

Phenolphthalein is the most suitable for the titration of all weak acids, both in aqueous and in alcoholic solution. In the latter case, however, blank experiments should always be performed to determine the acidity due to the amount of alcohol present and also to compensate the effect of the alcohol on the indicator exponent.

Chromic acid and chromates may be titrated, the end point occurring after the formation of chromate. Sulphurous acid may also be titrated to the normal sulphite, and dihydrion to monohydrion orthophosphate. The total acid in salts of weak bases, such as aniline, alkaloids, etc., may also be determined, as also in salts of aluminium and zinc. In the latter case time must be allowed for the alkali which is carried down by the precipitate to diffuse into the solution. The titration is complete when there is no reddening after several minutes.

*Tetrabromphenolphthalein.* See pp. 115, 295.

$p_I = 8.$

−0·3 —— 8 —— 12

colourless violet fades rapidly.

DIAGRAM VI.

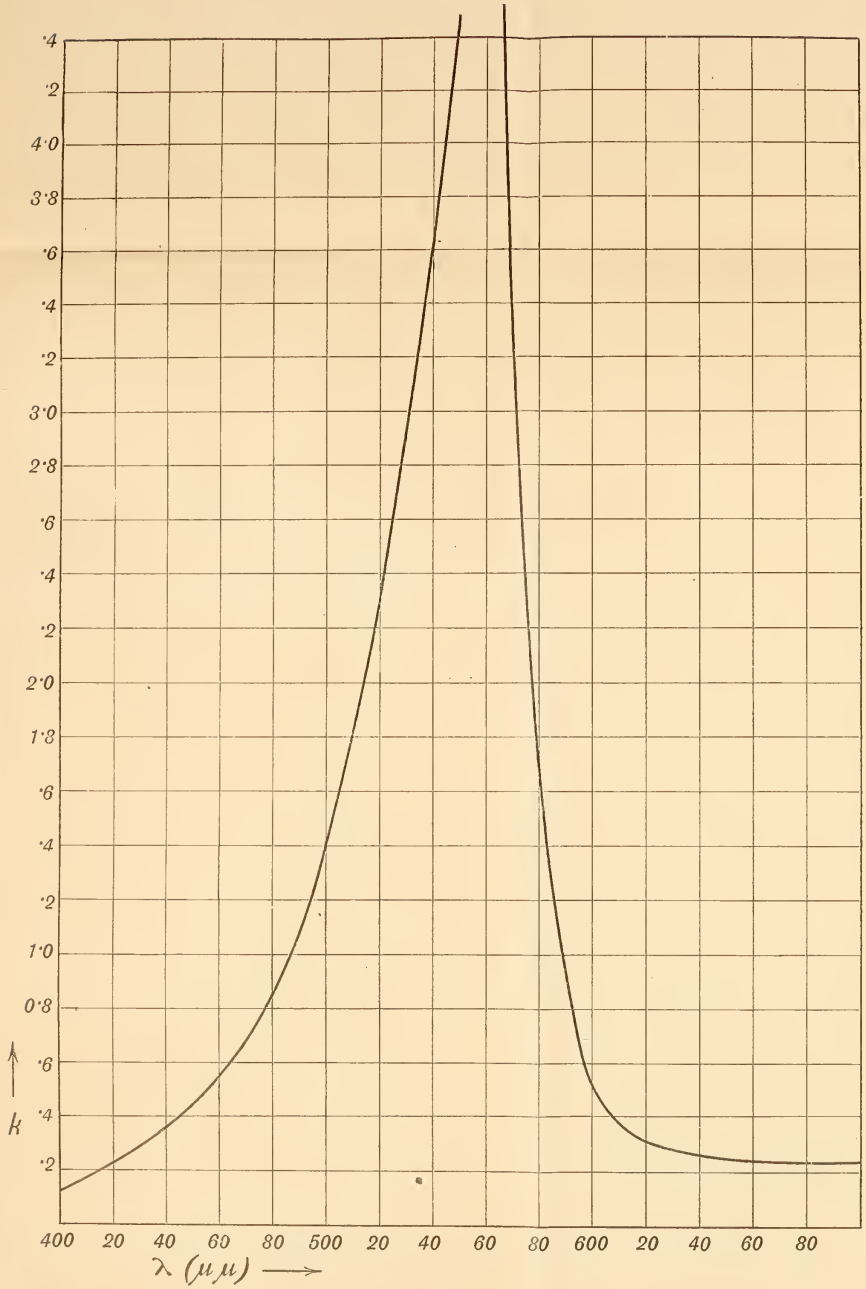



TABLE VI.

(6) *Phenolphthalein.*

0·005 per cent. 0·001 N. NaOH + 0·25 per cent. ethyl alcohol.

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| λ = 440 | 50 | 60 | 70 | 80 | 90 | 500 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 600 |
| *k* = 0·35 | | 0·53 | | 0·81 | 1·02 | 1·37 | 1·81 | 2·37 | 2·89 | 3·57 | 4·52 | 5·22 | 3·16 | 1·68 | 0·90 | 0·51 |
| λ = 680 | | | | | | | | | | | | | | | | |
| *k* = 0·25 | | | | | | | | | | | | | | | | |

DIAGRAM VII.

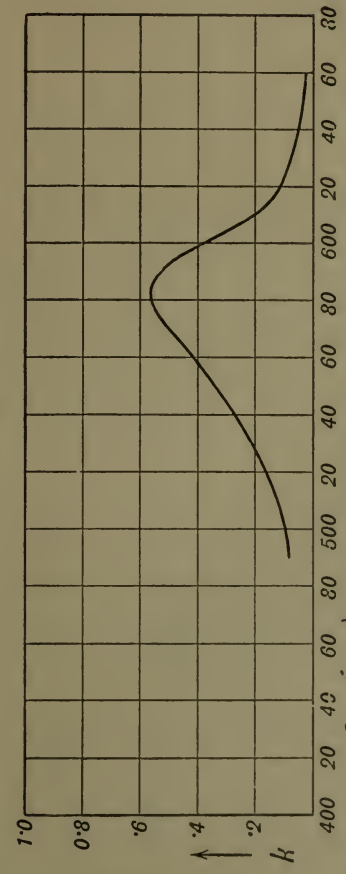



TABLE VII.

(7) *Tetrabromphenolphthalein.*

0·1 per cent. in 0·01 N. NaOH + 5 per cent. methyl alcohol.

The sample probably contained some more highly brominated molecules.

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| λ = | 490 | 510 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 600 | 10 | 20 | 60 |
| *k* = | 0·08 | 0·12 | | 1·20 | | 1·35 | 1·41 | 1·50 | 0·56 | 0·55 | 0·40 | 0·22 | 0·12 | 0·02 |

*Preparation.*—A mixture of 10 parts of bromine with 10 parts of glacial acetic acid is added to the phenolphthalein (5 parts) dissolved in four times its weight of hot alcohol. The compound is less soluble in alcohol than phenolphthalein is, but dissolves in ether, from which it may be recrystallised. The violet colour produced by alkalies is destroyed again by an excess.

DIAGRAM VIII.

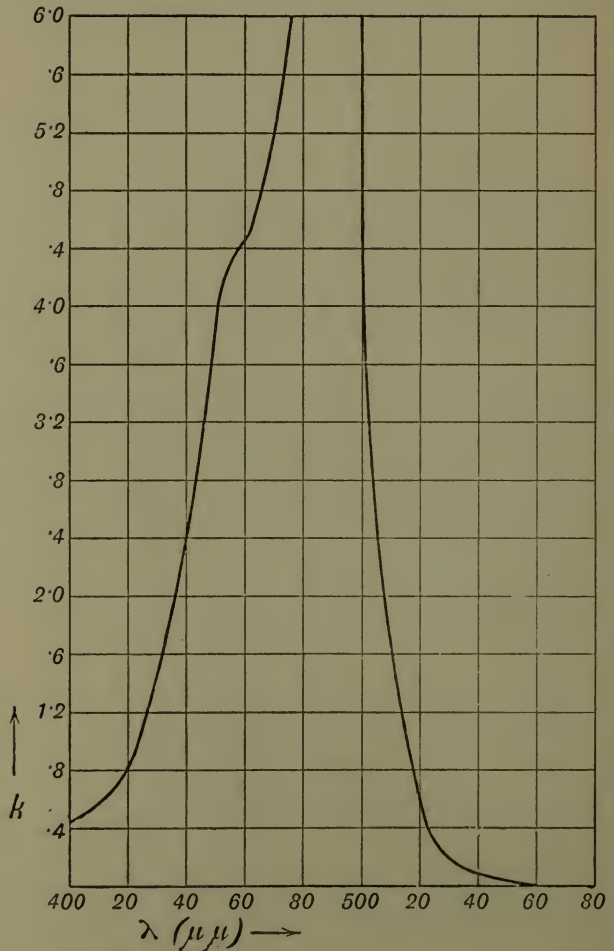


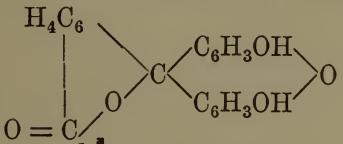

TABLE VIII.

(8) *Fluorescein.*

0·01 per cent. in 0·091 N. NaOH.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $\lambda$ = 400 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 510 |
| $k$ = 0·43 | 0·59 | 0·82 | 1·45 | 2·36 | 3·83 | 4·43 | 5·31 | 1·60 |
| $\lambda$ = 20 | 30 | 40 | | | | | | |
| $k$ = 1·62 | 1·18 | 0·09 | | | | | | |

*Fluorescein*, resorcin phthalein or uranine.

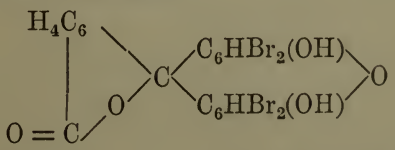


0 ——————— 5 ——————— 14

green-yellow green fluorescent.

*Preparation.*—Phthallic anhydride and resorcinol in the proportion of about 1 mol of the former to 2 of the latter are ground in a mortar and heated in an oil bath to nearly 200°. Powdered fused zinc chloride (about $\frac{1}{5}$ of the total weight) is added with stirring. The temperature is then kept at 210° until the mixture is solid. It is cooled, dissolved in dilute sodium hydroxide and the fluorescein is precipitated with hydrochloric acid. It is purified by extraction with hot alcohol, in which the compound is only slightly soluble. A 0·1 per cent. solution in alcohol may be made, and to this an equal volume of water added. A very small amount of the solution is used. The fluorescence is rather more easily seen by artificial light than by daylight, and is also visible in dark-coloured solutions. In turbid solutions, however, the indicator is useless.

*Eosin*, bromofluorescein.



Acids. Neutral or alkaline solutions.

yellow. green and fluorescent.

*Preparation.*—By acting on fluorescein with bromine in glacial acetic acid. Or bromine is added to the fluorescein suspended in ethyl alcohol, and the precipitate is washed

DIAGRAM IX.

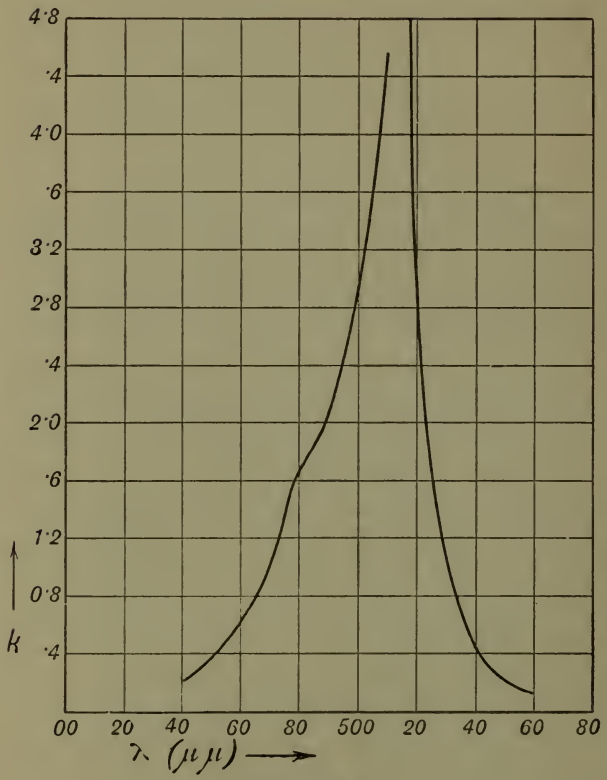



TABLE IX.

(9) *Eosin in Alkali.*

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $\lambda$ = 440 | 50 | 60 | 70 | 80 | 90 | 500 | 10 | 20 |
| $k$ = 0·21 | 0·37 | 0·64 | 1·10 | 1·67 | 2·10 | 2·93 | 4·55 | 2·76 |
| $\lambda$ = 30 | 40 | 50 | 60 | | | | | |
| $k$ = 1·02 | 0·48 | 0·21 | 0·13 | | | | | |

and converted into the sodium salt. The compound may be recrystallised from alcohol and is used in the form of the sodium salt in aqueous solution. It may also be used in the titration of dark solutions.

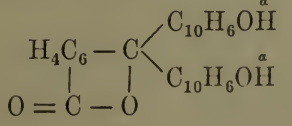
*Iodeosin*, dianthin, erythrosin, tetraiodfluorescein. Formula is analogous to that of eosin.

| — 0·3 | 0 —— 14 |
|---|---|
| green-yellow | pink. |

*Preparation.*—By treating an alkaline solution of fluorescein with an alkaline solution of iodine, and adding glacial acetic acid. The commercial sodium salt may be purified by recrystallisation from alcohol, then dissolved in water, precipitated by HCl, washed and dried. It is a red powder, almost insoluble in chloroform, water, and cold alcohol, but soluble in hot alcohol or aqueous ether. The alkali salts are scarcely fluorescent.

It has been applied by Forster and Mylius to the detection of small quantities of alkalies, such as are dissolved by water from glass. Some ether is made neutral by shaking first with dilute alkali, then with water. In a litre of this a few milligrams of the indicator are dissolved, and 10 to 20 c.c. of this solution are added to about 100 of that which is to be tested. The aqueous layer is coloured pink by traces of alkali. If excess of 0·001 acid is added the ethereal layer becomes yellow, and the alkali originally present may be found by titrating back with 0·001 N. alkali.

α *Naphtholphthalein* (Grabowski, 1871).



Range 7·3 to 8·7 (Sorensen).

| 7 | 8 | 9 |
|---|---|---|
| reddish | greenish | blue. |

*Preparation.*—Sorensen and Palitzsch, *Biochem. Zeitsch.*, 24, 380 (1910). *a* Naphthol, 36 grams ($\frac{1}{4}$ mol and phthallyl chloride, 25·4 grams ($\frac{1}{8}$ mol), are rubbed together in a 2 litre porcelain basin, allowed to stand for a quarter of an hour at room temperature, then for half an hour on a gently boiling and for half an hour on a briskly boiling water bath. The mass becomes more viscous and is strongly rubbed together at intervals. One litre of 0·2 N. sodium hydroxide is then added. A blue solution is formed and a red brown mass remains undissolved. It is heated for a further quarter of an hour on the water bath at 100°, the molten residue being well stirred. It is then cooled and the solid residue is filtered off and washed. It is then powdered, 1 litre of 0·1 NaOH is added, and the mixture is gradually raised to 100° on the water bath with good stirring. The blue solution is added to the former. The residue is extracted twice again in a similar manner, with the same amount of sodium hydroxide. The last residue should weigh about 15 grams. The solution is treated with 400 c.c. of N/2 HCl which gives no precipitate, and carbon dioxide is passed. The *a* naptholphthalein comes down as a bulky red precipitate, and phthallic acid remains in solution. The reddish mother liquor is sucked off and the solid dye well washed with water containing carbon dioxide. This solid may be further purified by dissolving in $\frac{1}{2}$ to $\frac{4}{10}$ N. baryta, filtering and acidifying slightly with hydrochloric acid, washing free from chlorides with water and drying in air. The yield is about 11 grams, but this still contains a less soluble substance which gives a green with alkalies. This may be separated by extraction in a Soxhlet apparatus with benzene, the first extract being thrown away. On further extraction the *a* naptholphthalein collects as a crystalline crust in the flask. It is inclined to stick in the extraction shell, but may be obtained by dissolving in alcohol, evaporating to

Diagram X.

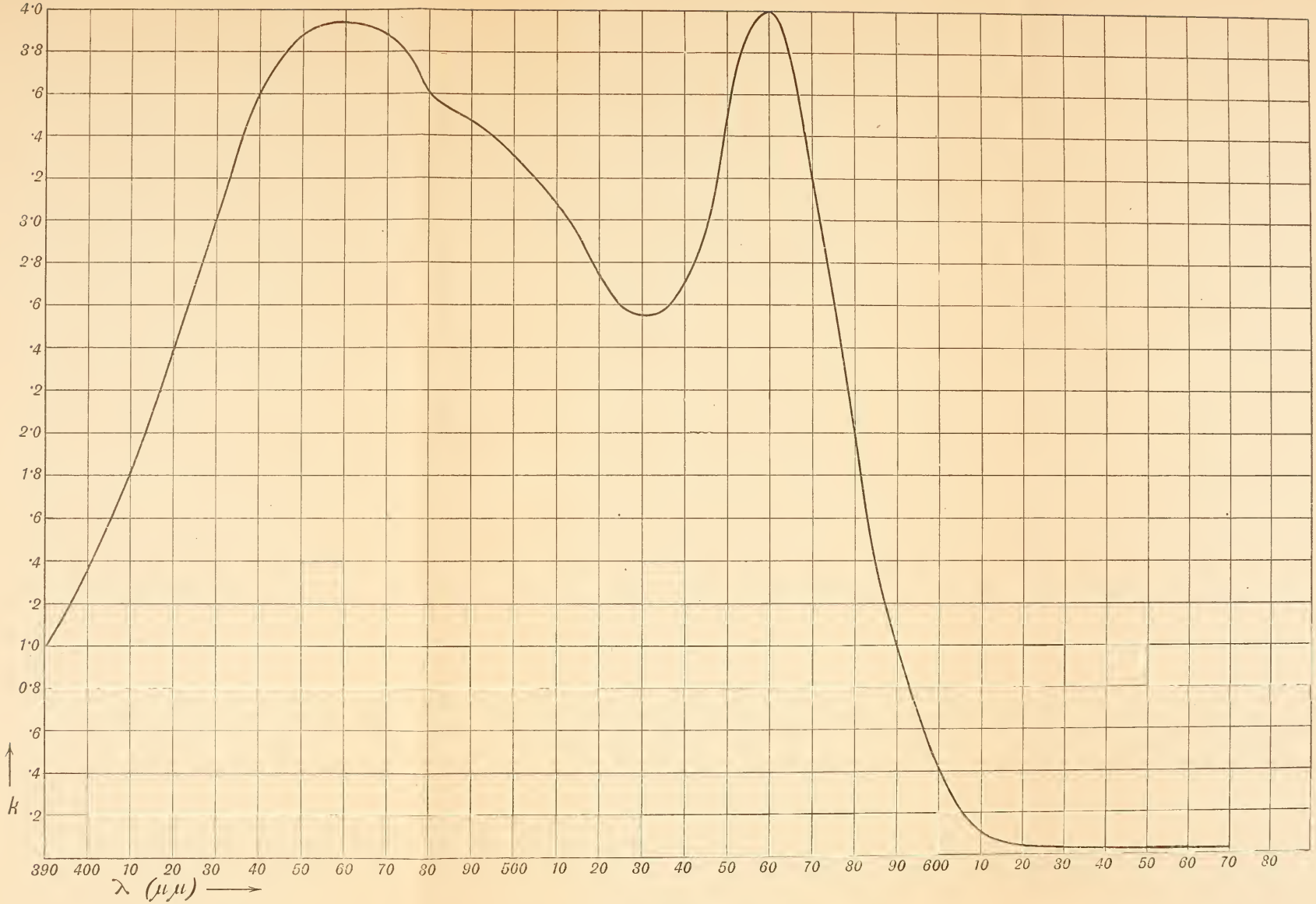



Table X.

(10) *p. Rosolic Acid.*

0·025 per cent. in 0·001 N. NaOH + 7·5 per cent. of methyl alcohol.

| | | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| λ = | 400 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 500 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 600 | 10 | 680 |
| *k* = | 1·38 | 1·85 | 2·39 | 3·02 | 3·60 | 3·93 | 3·95 | 3·90 | 3·60 | 3·50 | 3·30 | 3·10 | 2·75 | 2·55 | 2·70 | 3·50 | 4·00 | 3·30 | 2·00 | 1·00 | 0·44 | 0·13 | 0·04 |

dryness, powdering and again extracting with benzene. The process is continued until the residue in the shell, when dissolved in alcohol and diluted with alkali, gives a green and not a blue colour.

The crystals obtained are dissolved in alcohol, evaporated to dryness, rubbed up with benzene and washed by decantation, then dried in a vacuum at 100° to 110°. The drying frees it from 1 mol of benzene of crystallisation.

The stock solution contains 0·1 gram in 150 of alcohol and 100 of water, and of this 4 to 12 drops are added to 10 c.c.

It is not affected by small amounts of toluol or chloroform, larger amounts remove it from the aqueous solution. It is scarcely affected by the degradation products of proteins, but true proteins tend to destroy the colour.

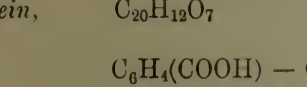
The fact that its useful range includes a lower exponent than that of phenolphthalein renders it a most useful supplement to the latter in testing sea water or dilute carbonates.

*Thymolphthalein.*

| 10 | 11 |
|---|---|
| colourless | blue. |

*Preparation.*—Thymol and phthallic acid (equal weights) are heated together to about 150°. After action has ceased the mixture is cooled and washed with dilute hydrochloric acid, then water, and then petroleum spirit. The compound may be recrystallised from ether alcohol, and when pure melts at about 253°. A 0·5 per cent. solution in alcohol may be used.

*Gallein*, $C_{20}H_{12}O_7$



or anthracene violet, alizarin violet, pyrogallol violet

| — 0·3 to 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|
| orange | yellow | red-yellow | orange | red |

| 6 to 10 | 11 to 13 | 14 |
|---|---|---|
| red-violet | blue-violet | blue. |

*Preparation.*—Phthallic anhydride (1 mol) is heated with pyrogallol (2 mols) to about 200°. The melt is treated with water, then dilute alkali, dissolved in sodium hydroxide, and reprecipitated by acids. It may be purified by repeated solution in alcohol and precipitation by water. The compound appears as brilliant green crystals or a brownish powder, which dissolves readily in hot alcohol, giving a brown solution. It is only slightly soluble in cold organic solvents or water, but the sodium salt easily dissolves, giving a red colour and blue with excess of alkali. The stock solution may be made by dissolving 1 part in 100 of alcohol and adding an equal volume of water. The colours are not stable. It might find an application as a chameleon indicator for the rapid determination of hydrion concentrations (see Chap. V., p. 160).

*Rosolic Acid.*

$$O=C_6H_4=C\begin{matrix}\diagup C_6H_4OH \\ \diagdown C_6H_3(CH_3)OH\end{matrix}$$ Rosolic acid

$$O=C_6H_4=C\begin{matrix}\diagup C_6H_4OH \\ \diagdown C_6H_4OH\end{matrix}$$ Pararosolic acid.

Aurin or corallin.

Range 6 — 7, 6·9 — 8·0 (Sorensen).

$p_1 = 7{\cdot}96$ (Salm) 7·5.

| 6 | 7 | 8 |
|---|---|---|
| brownish | pink | red. |

DIAGRAM XI.

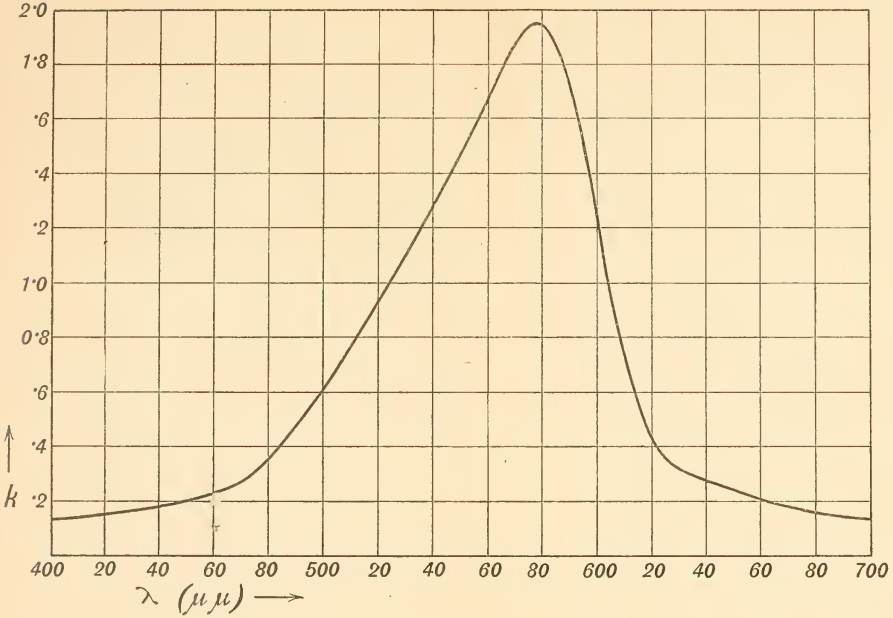



TABLE XI.

(11) *Methyl Violet* 6 *B*.

1/100,000 neutral.

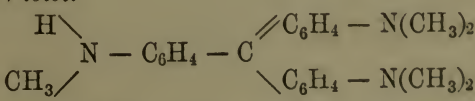
| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| λ = 400 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 500 | 10 | 20 | 30 |
| *k* = 0·13 | 0·14 | 0·15 | 0·17 | 0·19 | 0·20 | 0·22 | 0·26 | 0·35 | 0·47 | 0·60 | 0·75 | 0·92 | 1·10 |
| λ = 40 | 50 | 60 | 70 | 80 | 90 | 600 | 10 | 20 | 30 | 40 | 50 | 60 | 70 |
| *k* = 1·28 | 1·45 | 1·65 | 1·85 | 1·95 | 1·75 | 1·28 | 0·74 | 0·43 | 0·32 | 0·27 | 0·23 | 0·20 | 0·17 |
| λ = 80 | 90 | 700 | | | | | | | | | | | |
| *k* = 0·16 | 0·15 | 0·14 | | | | | | | | | | | |

*Preparation.*—The leuco bases of the corresponding rosanilines are treated with nitrous acid in concentrated hydrochloric acid and boiled with water, whereby OH takes the place of $NH_2$. Or 6 parts ef phenol, 3 of sulphuric acid, and 4 of anhydrous oxalic acid are heated for 24 hours to 120° or 130°. The residue after treatment with hot water is dissolved in alcohol and ammonia gas is passed in. The precipitate is boiled with hydrochloric acid. It forms dark-red crystals with a greenish lustre. It is insoluble in water but soluble in alcohol, from which it may be crystallised. It forms a colourless compound with potassium bisulphite.

The stock solution may contain from 0·5 to 1 per cent. of the indicator in 50 per cent. alcohol.

The colour change is not highly conspicuous, and is less so by artificial light. It may be used for testing natural waters, as the alkalinity due to bicarbonates is sufficient to turn it pink, while the presence of much free carbon dioxide is shown by a brownish colour.

*Methyl Violet.*



The chloride of pentamethyl triamino triphenyl carbinol, with varying amounts of the tetra and hexa methyl derivatives.

Range 0·1 to 3·2 (Sorensen).

| −0·3 | 0 | 1 | 2 | 3 to 13 |
|---|---|---|---|---|
| yellow | yellow-green | green-blue | blue violet | violet fades. |

*Preparation.*—Dimethylaniline is heated with copper sulphate or nitrate, sodium chloride, and a little acetic acid or phenol. The product is extracted with dilute sulphuric acid, then salted out with sodium sulphate, dissolved in water, and reprecipitated with sodium chloride.

It forms green lustrous lumps or green powder. It is soluble in water and alcohol, moderately in benzene, scarcely in ether. Sodium hydroxide gives a violet-brown precipitate which is soluble in ether. Methyl violet is a typical acid insensitive indicator and is suitable for detecting strong acids in the presence of weak acids.

*Benzaldehyde Green*, or malachite green,

$$C_6H_5 - C\begin{matrix} = C_6H_4 = N(CH_3)_2 \\ \backslash C_6H_4 - N(CH_3)_2, \end{matrix}$$

the hydrochloride or oxalate of diamino triphenyl methane.

| 0 | 1 | 2 | ⟶ 12 ⟶ | |
|---|---|---|---|---|
| yellow-brown | green | blue | blue | fades. |

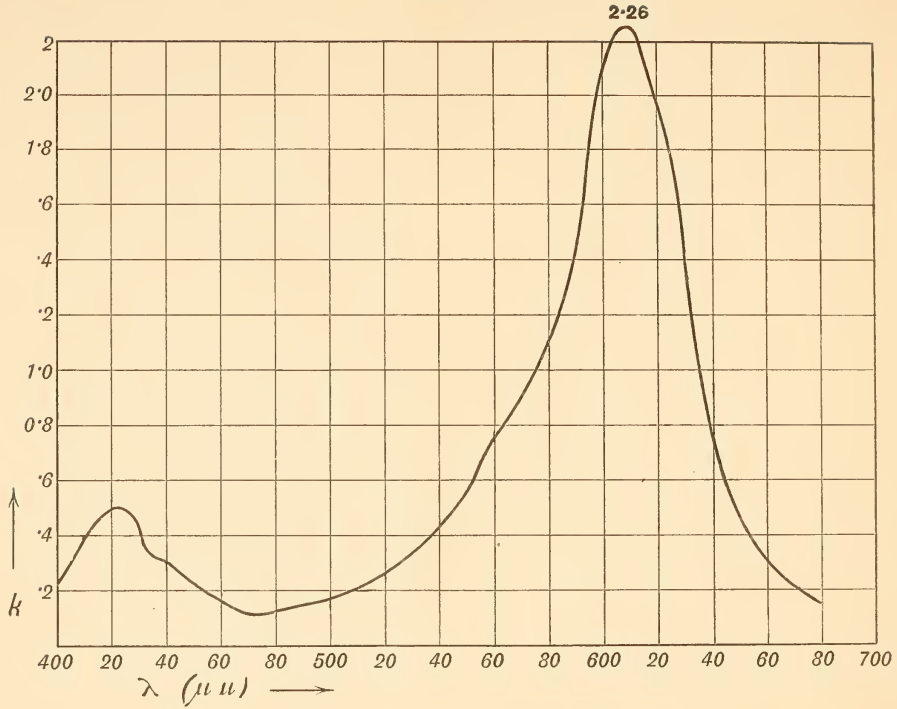
*Preparation.*—Dimethylaniline is mixed with about half its weight of benzaldehyde and its own weight of concentrated hydrochloric acid. The mixture is kept at 100° for about 24 hours in a flask fitted with a reflux condenser. It is then made alkaline and any unchanged reagents are removed in a current of steam.

The solid leuco base is washed free from alkali, melted at 100° in a porcelain basin, and dissolved in a mixture of concentrated HCl and 30 to 40 per cent. acetic acid.

For every 10 parts of solid base 2·7 parts of pure anhydrous HCl and 4 parts of pure acetic acid are required. Excess of water and then a paste of lead peroxide* (of which 7½ grams are needed for each 10 grams of base) are added gradually to the cooled solution. After stirring well the excess of $PbO_2$ is filtered off and the lead in solution precipitated with $Na_2SO_4$. The solution is then filtered and boiled and the base is precipitated with sodium

* The $PbO_2$ is prepared by oxidising lead acetate with bleaching powder. The percentage of $PbO_2$ in the paste is determined by means of oxalic acid.

## Diagram XII.




## Table XII.

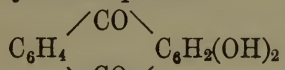
(12) *Malachite Green.*

1/50,000 neutral.

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| λ = 410 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 500 | 10 | 20 | 30 | 40 |
| *k* = 0·40 | 0·50 | 0·42 | 0·31 | 0·23 | 0·16 | 0·11 | 0·13 | 0·15 | 0·17 | 0·22 | 0·26 | 0·36 | 0·44 |
| λ = 50 | 60 | 70 | 80 | 90 | 600 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 |
| *k* = 0·57 | 0·76 | 0·92 | 1·11 | 1·50 | 2·10 | 2·26 | 1·97 | 1·40 | 0·82 | 0·45 | 0·31 | 0·22 | 0·15 |

hydroxide. It is filtered, washed, and dried, and may be further purified by dissolving in petroleum ether, filtering and evaporating the solvent. Or it may be precipitated as the monochloride, zinc chloride double salt, by the addition of saturated zinc chloride and sodium chloride to the filtrate from the lead sulphate.

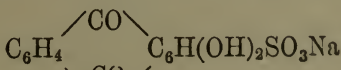
*Alizarin*, or dioxy-anthraquinone.



| 0—5 | 6 | 7—11 | 12—13 | 13— |
|---|---|---|---|---|
| green-yellow | brown-yellow | lilac | violet | blue. |

*Preparation.* — Sodium anthraquinone sulphonate is heated with sodium hydroxide, and potassium chlorate and water in an autoclave at about 200°. The solid product may be dried at 120° or sublimed. Or the dye may be extracted from madder root by boiling with acids which split up the glucoside. It forms orange crystals with 3 mols of water, which are soluble in hot water and the ordinary organic solvents. A 0·5 per cent. alcoholic solution may be used.

*Sodium Sulphalizarate*, alizarin red S (B).



Range 3·7 (yellow) — 4·2 (pink) (Walpole).

| 0—4 | 5 | 6—11 | 12—14 |
|---|---|---|---|
| yellow-green | brown | red | violet. |

Principal changes at 4 to 5 and 5 to 6 (Salm).

*Preparation.*—The acid is prepared by sulphonating alizarin with fuming sulphuric acid. A 1 per cent. solution

DIAGRAM XIV.

*Safranin.*

1 Lilac — 2 pink — pink — 14 violet to colourless — 15 colourless

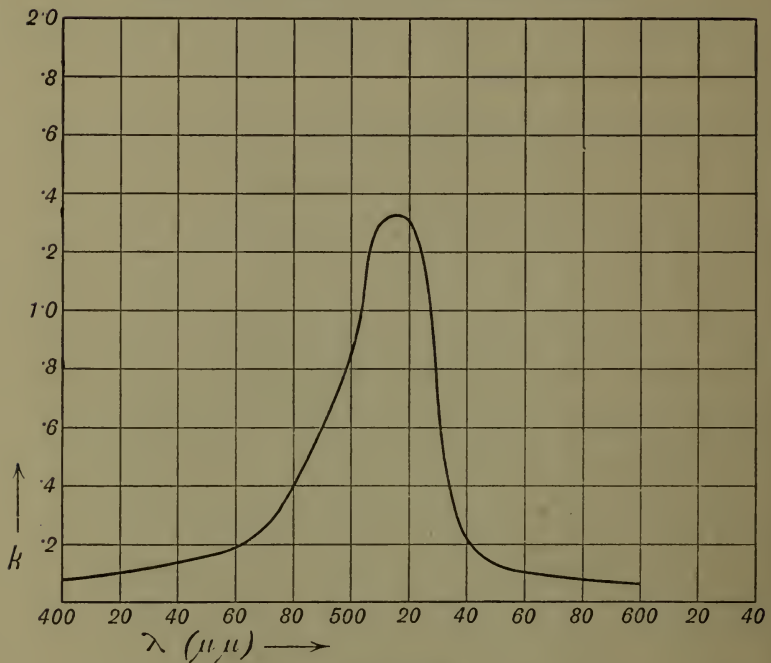



TABLE XIV.

(14) *Safranin.*

0·005 per cent. neutral.

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| λ = 400 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 500 |
| *k* = 0 08 | | 0·10 | | 0·15 | | 0 19 | 0·26 | 0·40 | 0·60 | 0·83 |
| λ = 10 | 20 | 30 | 40 | 50 | 60 | 600 | | | | |
| *k* = 1·29 | 1·30 | 0·76 | 0·20 | | 0·09 | 0·05 | | | | |

in water may be used after filtration. This indicator has been recommended for use in place of methyl orange by Knowles (see Walpole, p. 160). The colour change is well marked by artificial light. It fails in the presence of borates, which impart a yellow or brown colour.

DIAGRAM XIII.

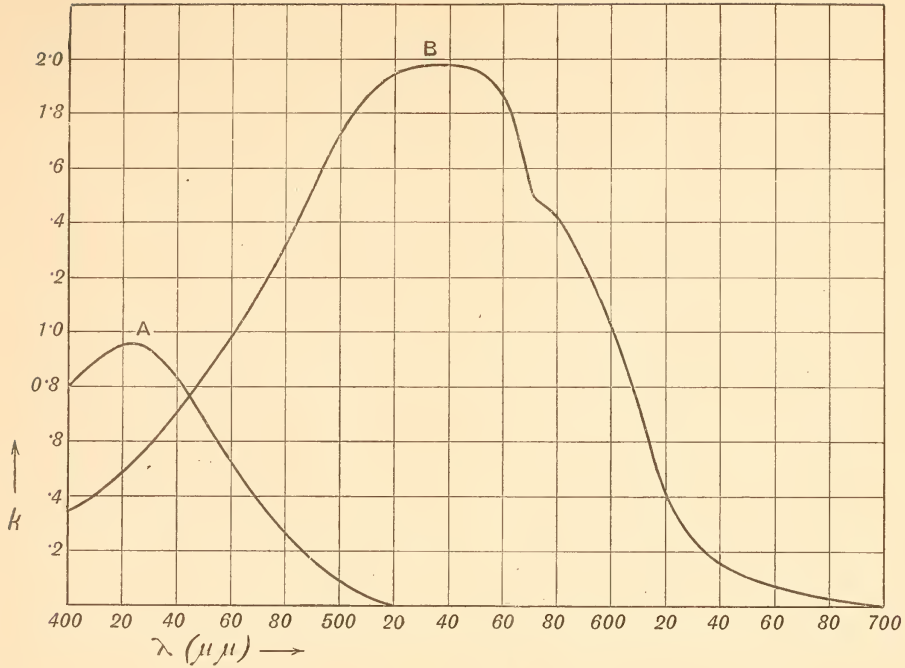


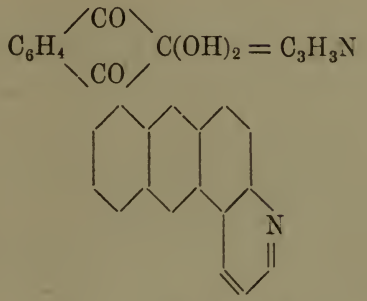

TABLE XIII.

(13) *Alizarin.*

A 1/10,000 0·001 N. HCl.
B 3/100,000 0·001 N. NaOH.

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| λ = | 400 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 500 | 10 | 20 | 30 | 40 |
| *k* (A) = | 0·80 | 0·88 | 0 96 | 0·93 | 0·83 | 0·70 | 0·54 | 0·38 | 0·27 | 0·16 | 0·07 | | | | |
| *k* (B) = | 0·35 | 0·40 | 0·49 | 0·60 | 0·72 | 0·83 | 1·03 | 1·16 | 1·38 | 1·53 | 1·73 | 1·85 | 1·95 | 1·97 | 1·98 |
| λ = | 50 | 60 | 70 | 80 | 90 | 600 | 10 | 20 | 30 | 80 | | | | | |
| *k* (B) = | 1·98 | 1·87 | 1·50 | 1·42 | 1·25 | 1·02 | 0·72 | 0·41 | 0·25 | 0·03 | | | | | |

*Alizarin Blue S*, the sodium bisulphite compound of alizarin S.



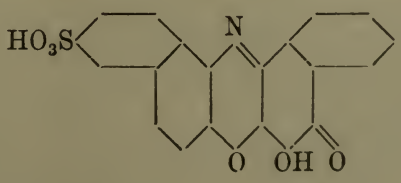
| 0—6 | 7 | 8—11 | 12 | 13 | 14 |
|---|---|---|---|---|---|
| pale yellow | green-yellow | green | violet | blue | blue-green. |

The most marked changes are from 11 to 12 and from 12 to 13.

*Preparation.*—*β* nitro-alizarin is prepared by treating alizarin in glacial acetic acid with nitric acid. It forms orange-yellow needles which melt at 244° and can be sublimed. This is then heated with glycerine and sulphuric acid.

The product forms brownish-violet needles insoluble in water and difficultly soluble in alcohol or ether. The melting point is 270°.

*Alizarin Green B* (Formanek's indicator).



| − 0·3 | 0—11 | 12 | 13—14·3 |
|---|---|---|---|
| blue | flesh-coloured | yellow | green. |

The most marked changes are at $-0{\cdot}3$ to $1{\cdot}0$ and 12 to 13.

*Preparation.*—By heating $\beta$ naphtho-quinone sulphonic acid with 2 amino, 1 naphthol, 4 sulphonic acid in alkaline solution. It is a dark greenish substance, soluble in water, less soluble in alcohol.

*Diortho-hydroxy styrilketone*, lygosin (Aron, *Pharm. Post*, 46, 521 (1913); see Walpole, p. 160).

$$OC = (CH = CH - C_6H_4OH)_2$$

Range $7{\cdot}3$ to $8{\cdot}7$.

| Acid. | Alkaline. |
|---|---|
| brown-yellow | green. |

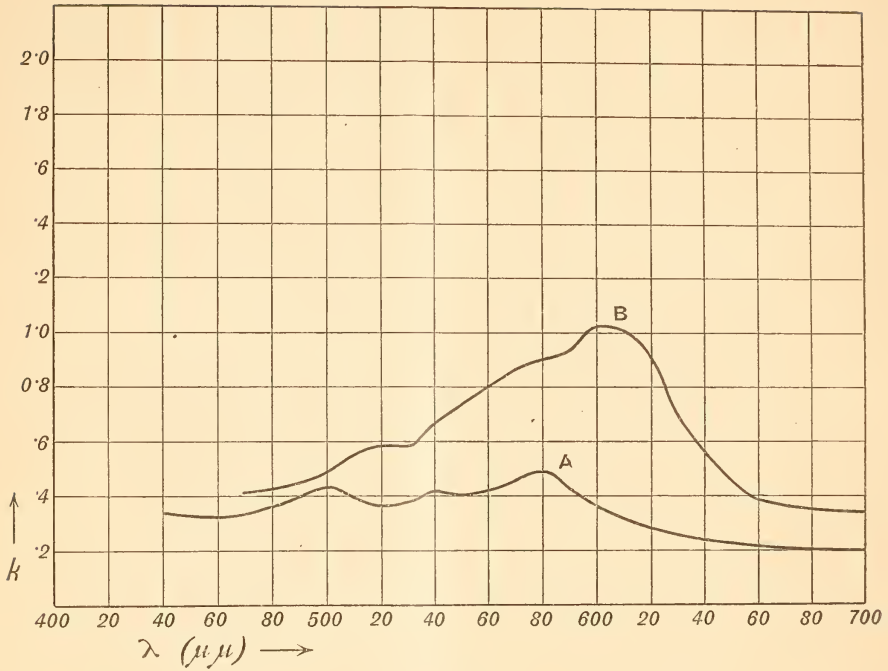
The colour fades after a few hours, unless the solution contains borates, which preserve the colour.

*Litmus.*—A neutral point indicator with a wide range from 5 to 8. The half-way change is at about $6{\cdot}5$.

*Preparation.*—The commercial product is prepared by the fermentation of lichens with ammonia and potash. The cubes are made up with chalk and gypsum. It contains various colouring matters, the most important of which is azolitmin, obtained by the process mentioned below.

The colouring power of the crude sample may be tested by grinding up and digesting with cold water for a day or two. The colour is compared with that produced by a specimen of known quality. An aqueous extract made in this manner may be siphoned off and used directly, but it gives a violet colour instead of a pure blue with alkalies. The sensitivity is tested by colouring 250 c.c. of water a neutral violet and then adding 1 drop of N/10 acid or 1 drop of N/10 alkali. The colour should be changed to pure red or pure blue respectively. The purification of litmus consists in the partial isolation of azolitmin, a dark brown

## Diagram XV.




## Table XV.

(15) *Litmus.*

A 0·1 per cent. 0·001 N. HCl.
B 0 1 per cent. 0·001 N. NaOH.

The general absorption shows a colloidal solution.

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| λ = 440 | 50 | 60 | 70 | 80 | 90 | 500 | 10 | 20 | 30 | 40 | 50 | 60 | 70 |
| *k* (A) = 0·34 | | | 0·33 | 0·38 | 0·39 | 0·43 | 0·39 | 0·36 | 0·37 | 0·41 | 0·40 | 0·41 | 0·45 |
| *k* (B) = | | | 0·41 | | | 0·48 | 0·55 | 0·58 | 0·58 | 0·67 | 0·72 | 0·80 | 0·87 |
| λ = 80 | 90 | 600 | 10 | 20 | 30 | 40 | 50 | 60 | 700 | | | | |
| *k* (A) = 0·49 | 0·43 | 0·36 | 0·29 | 0·26 | | 0·23 | | | 0·20 | | | | |
| *k* (B) = 0·90 | 0·93 | 1·02 | | 0·91 | | 0·57 | | 0·38 | 0·34 | | | | |

powder which is insoluble in alcohol but slightly soluble in water. It may be obtained from the crude material by various methods. The powdered substance may be extracted with hot alcohol, then with water. The excess of water from the aqueous extract is evaporated on a steam bath, and the colouring matter is reprecipitated with alcohol containing acetic acid. This process is repeated as often as necessary (Mohr and Wartha).

Or the cold water extract may be precipitated with an excess of alcohol with some HCl upon pulped asbestos, washed with hot acidulated water until the washings give a pure blue with alkalies, then dissolved in dilute alkali (Glaser).

Litmus solution does not keep when acid and also undergoes a fermentation when air is excluded. It is best kept in bottles loosely plugged with cotton wool and with the addition of a little disinfectant (*e.g.*, phenol).

The colour change is most marked by daylight, but not so good by artificial light. By sodium light, however, the change from colourless (acid) to dark blue is conspicuous.

*Litmus Paper.*—The blue and red kinds are made by steeping paper in the acid or alkaline extract of the purified indicator. The paper is then dried in the air. In making the neutral paper the tint when freshly withdrawn from the solution should be rather red than blue, as it becomes bluer on drying.

*Turmeric.*

| Acid. | Alkaline. |
|---|---|
| pure yellow | brown. |

*Preparation.*—The roots of some plants belonging to the genus curcuma contain this colouring matter, which has to be freed from oily substances and also from another coloured substance which is easily soluble in water. They

may be steamed and extracted with $CS_2$ and then with ether. The product may be purified by recrystallisation from dry ether and forms yellow crystals melting at 178°, very slightly soluble in water, and soluble in organic solvents. A 0·5 per cent. solution in alcohol may be made. Or the root after maceration with water is dried and extracted with alcohol.

Turmeric paper is made by soaking in the dilute alcoholic solution. It is used to detect ammoniacal vapours, boric acid, and uranium salts, which all give a brown colour.

The extract of mimosa flowers is very similar in its properties to turmeric.

*Cochineal.*

$p_I = 5$ (Noyes).

| 0—4 | 5 | 6 |
|---|---|---|
| yellow | brown-pink | lilac. |

The principal change occurs from 5 to 6.

The whole insects (3 grams) are extracted with 250 c.c. of aqueous alcohol (20 to 25 per cent. alcohol). The tincture has a natural acid reaction and should be neutralised (to violet) before use with a very little ammonia. The colour change is conspicuous both by day and artificial light.

*Lacmoid*, or resorcin blue.

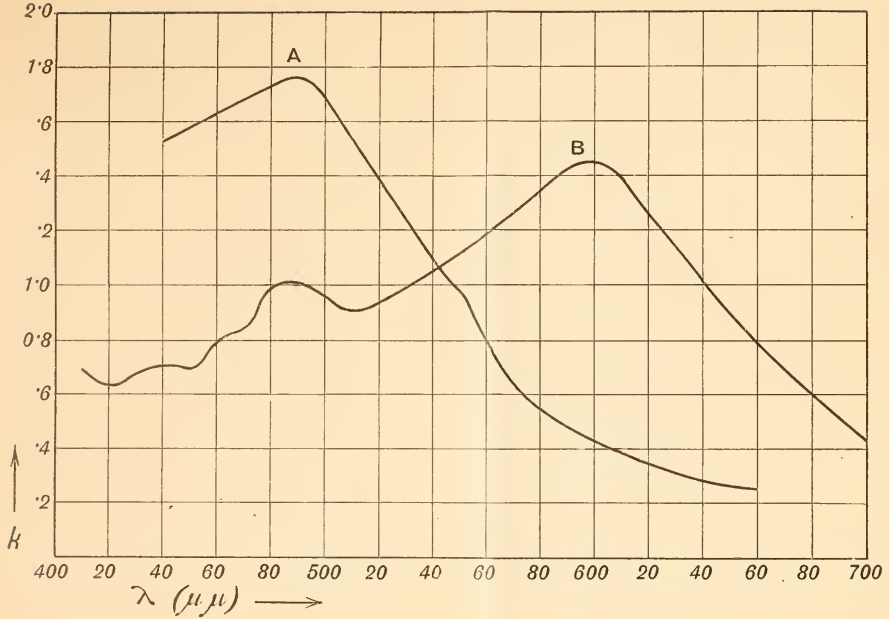
$C_{12}H_9O_3N$.

| 0—4 | 5 | 6 | 7 |
|---|---|---|---|
| pink | violet | violet-blue | blue. |

None of the changes are sharp.

*Preparation.*—Resorcin (20 parts), $NaNO_2$ (1 part), and water (1 part) are heated to 110° in an oil bath. The reaction will continue without further heating until the colour of the mass becomes pink. The heating is then continued up to about 120°, ammonia is evolved, and the colour becomes blue. The mixture is then dissolved in a

## Diagram XVI.




## Table XVI.

(16) *Lacmoid.*

A 1/4,000 0·001 N. HCl
B 1/8,000 0·001 N. NaOH } + 10 per cent. of methyl alcohol.

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| λ = 410 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 500 | 10 | 20 | 30 | 40 | |
| *k* (A) = | | | 1·53 | 1·58 | 1·63 | 1·67 | 1·73 | 1·76 | 1·67 | 1·53 | 1·38 | 1·24 | 1·08 | |
| *k* (B) = 0·70 | 0·64 | 0·69 | 0·71 | 0·70 | 0·80 | 0·84 | 1·00 | 1·01 | 0·96 | 0·90 | 0·95 | 0·98 | 1·05 | |
| λ = 50 | 60 | 70 | 80 | 90 | 600 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | |
| *k* (A) = 0·97 | 0·78 | 0·64 | 0·54 | 0·49 | 0·43 | 0·39 | | | | | 0·25 | | | |
| *k* (B) = 1·13 | 1·20 | 1·27 | 1·34 | 1·43 | 1·45 | 1·39 | 1·25 | 1·15 | 1·00 | | | | | |
| λ = 90 | 700 | | | | | | | | | | | | | |
| *k* (B) = | 0·43 | | | | | | | | | | | | | |

little water, hydrochloric acid is added until the colour is changed to pink, and the precipitate is washed with a little water and dried at 100°. It should be easily soluble in hot water, giving a pure blue solution. If the hot solution is again treated with HCl, etc., as above, a purer product is obtained. Or the crude preparation may be extracted with alcohol and the solvent evaporated in a vacuum.

A 0·2 per cent. solution in alcohol may be used. If it has a violet instead of a pure blue in alkaline solution this may be corrected by adding to the lacmoid a slightly greater quantity of naphthol green and making a 1 per cent. solution of the mixture in 30 per cent. aqueous alcohol.

In its colour changes it is similar to litmus, but is less sensitive to carbon dioxide. It is used for much the same purposes.

*Lacmoid Paper.*—The blue kind is made by adding dilute sulphuric acid to the alcoholic lacmoid solution until the paper is just coloured red, but turns to blue on drying. The red kind is first dipped in dilute sulphuric acid and then dried before being coloured with the strongly acid solution of the indicator. It must be kept airtight in dry bottles, as it is very sensitive to traces of alkali.

These papers can be used to detect dichromate in the presence of chromate. The former is acid to the blue, the latter alkaline to the red, paper. They are also useful in titrating alkali sulphides, since the hydrogen sulphide liberated would destroy the colour of the indicator if the latter were in solution.

*Phenacetolin.*

$C_{16}H_{12}O_2$.

| 0—3 | 4 | 5 | 6—10 | 11—12 | 12—14 |
|---|---|---|---|---|---|
| yellow | brown-yellow | brown-red | pink | violet | colourless. |

The change from 5 to 6 is well marked.

*Preparation.*—Phenol, concentrated sulphuric and glacial acetic acids (1 mol of each), are heated together for several hours under a reflux condenser. The product is washed with water and then consists of a brown compound which is easily soluble in hot water and a green compound which is less easily soluble. The former is the most useful indicator. It may be dissolved in water or alcohol, 0·2 to 0·5 per cent.

*Hæmatoxylin.*

$C_{16}H_{14}O_6$.

*Hæmatein.*

$C_{16}H_{12}O_6$.

These colouring matters are obtained from logwood or campeachy. Fresh raspings from a massive piece are extracted with aqueous ether, the solvent is evaporated, and the hydrate ($3H_2O$ or $1H_2O$) obtained by recrystallisation from the aqueous residue with a little ammonium bisulphite. A 0·5 per cent. solution in alcohol is used.

The hæmatoxylin so prepared is easily oxidised to hæmatein, the purple colour with alkalies changing to blue and then to brown. It gives specific colours (blue to red-violet) with the salts of heavy metals.

*Hæmatein.*

| 0 | 1 | 2—5 | 6 | 7 | 8 |
|---|---|---|---|---|---|
| pink | greenish | green-yellow | brown-red | lilac | violet. |

| 9—10 | 11 | 12 | 13—14 | 14·3 |
|---|---|---|---|---|
| red-violet | red-violet to brown | darker | dark red to brown | blue-violet. |

The changes from 0 to 1 and at 6 and at 11 are well marked.

The oxidation of the hæmatoxylin may be effected by simply allowing the logwood raspings to ferment in the air.

Or the ethereal solution of hæmatoxylin with a few drops of nitric acid may be exposed to air.

It forms dark green masses with a metallic lustre, which are slightly soluble in hot water and in alcohol and ether.

*α Naphtholbenzoin.*

$C_{54}H_{38}O_5$.

| 0—8 | 9 | 10 | 11—14 |
|---|---|---|---|
| brown-yellow | yellow | green | green-blue. |

The changes from 9 to 10 and 10 to 11 are well marked.

*Preparation.*—By allowing 2 mols of α naphthol to act upon 1 mol of benzo-trichloride, the reaction being controlled by the addition of small quantities of benzene. After standing for about a day the mixture is warmed to about 40° and the unchanged reagents are removed by steam distillation. The product is dissolved in alkali and reprecipitated with acid washed and dried.

A 1 per cent. solution in alkali may be made up and coloured green with a little alkali.

*Cyanine*, or quinoline blue.

$C_{29}H_{35}N_2I$.

| 0—6 | 7 | 8 | 9 |
|---|---|---|---|
| colourless | pale blue | blue | violet. |

The change from 7 to 8 is well marked.

*Preparation.*—Equal molecules of quinoline and lepidine are caused to react with alkyl iodides, and the product is treated with caustic alkalies. The crystals obtained are greenish and insoluble in cold water. A 1 per cent. alcoholic solution may be used.

*Poirrier's Blue.*

| 1—11 | 12 | 13—14 |
|---|---|---|
| blue | violet | pink. |

The change at 11 to 12 is well marked.

*Preparation.*—It is prepared by acting upon triphenyl

rosaniline with sulphuric acid. A 0·2 per cent. solution may be used.

It is suitable for the determination of high exponents by the match method.

*Salicylic Acid and Ferric Solution.*—A few drops of ferric chloride are added to a clear solution of salicylic acid in water or aqueous alcohol. Dilute alkali is then run in until the colour has just become red-brown. Or a stronger solution may be made by digesting ferric hydroxide with hot concentrated neutral sodium salicylate. Or ferric chloride is added to a 20 per cent. solution of sodium salicylate in water until a precipitate is produced. To one half of this solution sodium hydroxide is added until the colour is orange, and to the other half acid until it is red, and the two are mixed (see *Analyst*, 27, 36).

When this indicator is added to an acid, and standard alkali is run in, the violet colour gradually develops, becomes most intense just before neutrality, and then vanishes.

*Red Cabbage.*

| Acids. | Alkalies. |
|---|---|
| red-violet | green. |

The change interval is from 2 to 4·5 (Walpole).

The leaves are shredded and steeped in water or dilute alcohol.

The colour change is distinct, and the indicator is not affected by proteins or toluene.

*Eosine Methylene Blue.*—A mixture of equal mols of the two compounds dissolved in alcohol.

| — 0·3 | 0—2 | 3—13 | 14 | 14·3 |
|---|---|---|---|---|
| green | blue | blue-violet | violet | red-violet. |

The changes from — 0·3 to 0·0 and 14 to 14·3 are well marked.

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## Chart showing the Hydrion Exponents of some Standards of Acidity and Alkalinity.

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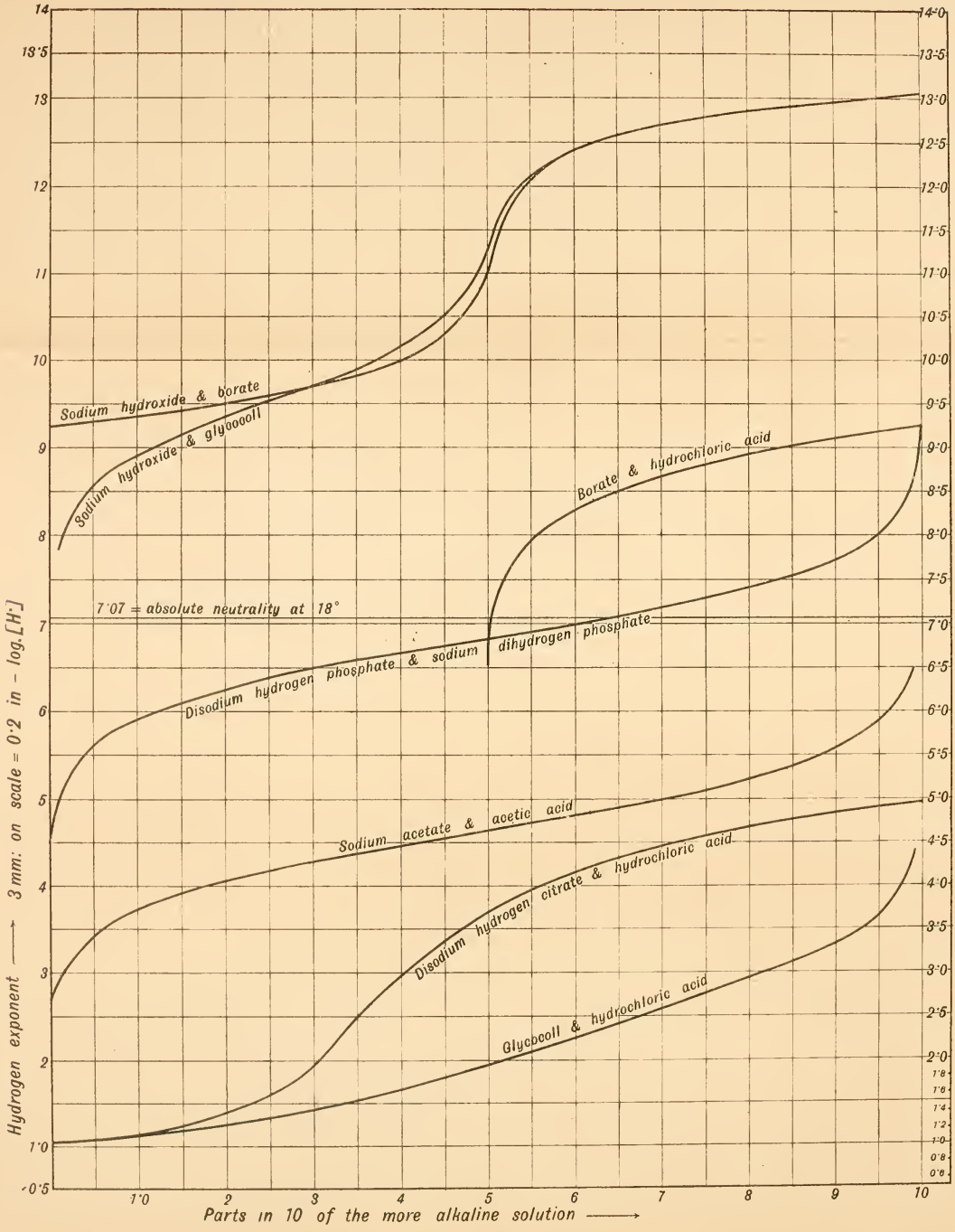
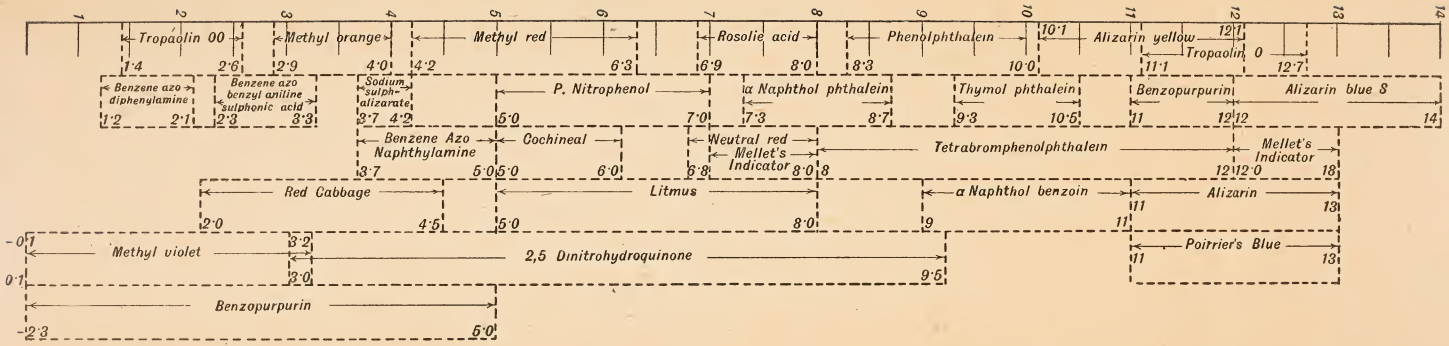
# Chart showing the Hydrion Exponents of some Standards of Acidity and Alkalinity.






CARD OF INDICATOR CHANGES FOR APPLICATION TO CHART AND NEUTRALISATION CURVES.